CHEMISTRY

A Textbook for Higher Secondary Schools

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A Textbook for Higher Secondary Schools

Classes XI-XII

Part II

विद्ययाऽमृतमश्नुते

एन सी ई आर टी
NCERT

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Foreword

The present book, *Chemistry—Part II*, is meant for Class XII students of academic stream under the 10+2 pattern of education The main features of the textbook are functionality, conceptual clarity and disciplinary approach suitable for the students who will pursue their higher education in academic and professional courses

The general guidelines for the present textbook were provided by an Editorial Board for Chemistry which consisted of Prof. R C Mehrotra (Chairman), Prof. C. N. R. Rao, Prof R P Rastogi, Prof. P. Gopalaraman, Prof. A. N. Bose (Convener), Prof. (Smt.) Shakti R Ahmed, Dr. R. D Shukla and Shri R. Joshi. The Council is indebted to them for their help and cooperation.

The present textbook was written by a team of authors consisting of Prof A. N. Bose, Prof. C N. R. Rao, Prof. R. P. Rastogi, Prof. P. Gopalaraman, Prof. R. D. Dua, Dr B. D. Khosla, Dr. K. V. Sane, Dr R. D. Shukla and Dr. Puran Chand. The final editing of the book was done by Dr. B. D. Khosla in collaboration with Prof. A. N Bose, Dr. R D. Shukla and Dr. Puran Chand. I am grateful to all the authors and editors. for undertaking the work and completing it in a short period of time

Any suggestion for improvement of the textbook is welcome.

SHIB K. MITRA

Director

National Council of Educational
Research and Training

New Delhi
May, 1978

Preface

Under the 10+2 pattern of education, syllabus in chemistry for the +2 stage was prepared by a team of experts in order to make the course relevant and meaningful in our situation This +2stage chemistry course can be considered as a bridge course between the secondary level of general education and college course of higher level of academic proficiency and also professional courses At the end of this +2 stage course, students will be eligible to choose any suitable professional or academic career of their choice. Therefore, it was really a very difficult task for curriculum designers and book writers to design the course and write the book in a way to suit the needs of various types of diversified courses after the +2 stage. However, the positive effort in this direction has been made and we have already prepared Part I of the textbook intended to provide a two-semester course of one academic year for Class XI students

The present Part II of the textbook meant for Class XII students has been prepared in conformity with the approach we have adopted in this direction for Class XI This book includes Units which are either extension of the Units given in Part I, e.g , *More about atoms, More about molecules, More about states of matter, etc* , or Units dealing with new concepts of higher degree of sophistication suiting the intellectual capacity of the students of this age-group. Similar to Part I of the text book, in Part II also an effort has been made to present chemistry as a unified subject. As such there is no traditional classification of the subject as inorganic, organic and physical Chemical principles developed in the beginning (in the first few Units in Part I as well as in Part II) are used throughout the textbook. We have presente the Units in a particular sequence considering an appropriate teaching-learning sequence. Teachers have freedom to choose the sequence of their own while teaching the material. However, in an unified or integrated study of the subject the degree of freedom is less than that in a non-integrated (like physical, inorganic and organic) study since necessarily most of the conceptual framework must be studied first. It is understood that Units given in Part I and II of this textbook should provide a good introduction of the varied facets of chemistry.

There are 21 Units in this Part II of the textbook. These Units are further divided into Sections and Sub-sections for easy references. As we know, these Units are mainly meant for academic stream but some of the Units could possibly serve as bridge Units for an easy switch-over from the academic to vocational stream and some of the Units may be useful for vocational stream also

We have not attached much importance to the formal mathematical developments of ideas but have tried to develop a feeling for the way in which variables under discussion are related. Similar to Part I SI Units are widely used and most of the physical constants are expressed in terms of mole or mole as a reference We have already included appendices on SI Units, physical constants and conversion factors in Part I A logarithm table is given at the end of this book Exercises at the end of each Unit are intended to assist the students to reinforce their understanding.

At first sight, it will appear that the text has somewhat more subject-matter than would be expected in one academic year but we feel this has definite advantages. The students entering the +2-stage after general education of ten years of schooling may not have adequate background in chemistry Therefore, in many instances, it has been decided to develop the subject-matter from the very fundamental. Certain areas, such as atomic and molecular structure, states of matter, nuclear chemistry, biochemstry are more of interdisciplinary nature. Some of these are described in physics course and some other find wide application in the field of biology However, there is emphasis for covering chemical aspects and avoid duplication in such Units For example, nuclear fission and nuclear fusion which are given in physics course of the +2 stage have been dropped from this book

As stated earlier, first few Units deal with basic principles of chemistry which are useful in the study of the properties of the elements and their compounds It is impossible to give equal coverage to all the elements; therefore, only selective elements of a particular group are discussed in detail. Study of the carbon compounds is based on functional groups The last two Units of this book, 'Biochemistry' and 'Chemistry in the Service of Man', mainly deal with application of chemistry. An attempt has been made to bring reality to the fact by citing several applications to illustrate how chemistry works in the service of man. Since last two Units follow the Units dealing with study of compounds of carbon, it is understood that the students will not have difficulty in understanding the factual information given in these Units However, we cannot expect from the students that they will be able to memorize and reproduce the complicated structural formulae of all the compounds given in these Units No doubt, students would be able to appreciate and recognize the complexity of organic molecules in the living system We do not expect that in examinations, questions on the structural formulae of such complex molecules should be asked.

There is an effort from our side to make the presentation simpler and readable Fully aware of our obligation to provide sufficient and adequate footing for professional and academic courses, we have included the minimum number of concepts which the students will easily assimilate. All the times, we asked ourselves over and over again the same question : 'What is it that a student need and should receive from the text he uses in his study of chemistry ?' How far we have been successful in this effort, only practising teachers and students will tell us.

It is a fact that this book was prepared in a very short time at our disposal and in spite of our best efforts there may be many discrepancies, for which the persons who edited the textbook finally are responsible. Any suggestion for the improvement of the textbook from the practising teachers will be highly appreciated,

We acknowledge with grateful appreciation assistance received from Dr (Smt) Kamalesh Mittal and Shri Sukhvir Singh. We acknowledge also suggestions and advice of those teachers who read nearly all the manuscript in a review workshop

—AUTHORS

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UNIT 1

More About Atoms

The atomic concept of matter was introduced by Dalton in order to provide a basis for the laws of chemical combination. The work of Avogadro and Cannizaro made it possible to determine relative atomic masses. The knowledge of atomic masses led to two further important developments in chemistry. Mendeleev proposed the Periodic Table. It was based on the idea that physical and chemical properties of elements are a periodic function of their atomic masses. On the other hand, the knowledge of atomic masses enabled chemists to determine formulae for molecules of substances. These in turn led to the concepts of valency and chemical bond formation. All through these developments the atom was regarded as a structureless particle. Later, it was established that the atom consists of electrons, protons and neutrons and that it has an internal structure. The protons and neutrons of an atom constitute a dense, massive, central core, called the *nucleus* of the atom. The electrons are distributed around the nucleus. Their distribution plan is called the *electronic structure* or *electronic configuration* of the atom. Since then attempts have been made to explain all chemical behaviour of atoms in terms of their electronic structures. The electronic structure of an atom implies information about: (i) the number of electrons in the atom, (ii) their distribution in space around the nucleus, and (iii) the relative energies of electrons in different locations.

The concept of electronic structure is rather difficult to grasp because the behaviour of electrons is very different from that of other objects around us. We shall concentrate in this Unit on a study of some aspects of the behaviour of electrons which could be only briefly discussed in Unit 2 of Part I of this book. The topics we cover now include the dual nature of particles in motion, the de Broglie equation, the uncertainty principle, and the consequent description of orbitals and the energy level scheme for electrons surrounding the nucleus

1.1 DUAL NATURE OF MATTER AND RADIATION

There are experiments which show that matter and radiations behave sometimes like particles and sometimes like waves. This feature is expressed by saying that matter and radiation have a dual behaviour—particle-like and wave-like. To understand this aspect, we must first know what are particle-like and wave-like behaviours.

A grain of sand is an example of a particle. If we drop a stone into a pond of water, we observe waves spreading out in circles. One may, thus, say that a particle exists at one point position at a time or is localized, while a wave is a spread out pattern and is said to be delocalized. However, by merely looking at a beam of electrons or a beam of light we cannot say whether it is made up of localized or delocalized components. We have, therefore, to explore the consequences of localization and delocalization. These consequences can be nicely illustrated by a simple experiment.

Imagine a wall which has two windows, A and B, side by side, as shown in Fig. 1.1 (a). Suppose you have a lot of tennis balls which you are throwing one at a time at the wall Fig. 1.1(b) If both windows are open, a ball can go to the other side of the wall either through A or B. It is obvious that for the ball to pass through the window, A, it does not matter whether the other window, B, is open or closed. Further, if there are two persons beyond the wall and if one of them catches a particular ball, then you can be sure that the other person could not catch the same ball at the same time. A little thinking shows that all these effects arise because of the localized or particle-like nature of a tennis ball.

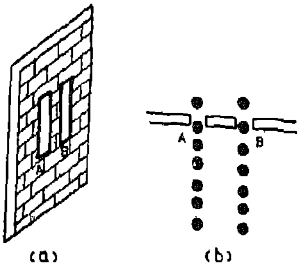


Fig. 1.1 (a) A wall with two windows, (b) Trajectories of balls.

Now, instead of throwing balls at the wall imagine that you are shouting at it. If both windows are open, the sound waves starting from you pass through both windows Anyone listening to you on the other side of the wall will not be able to tell whether the sound heard by him came through A or B. If this experiment were carried out by making the size of the windows and the spacing between them comparable to the wavelength of sound waves, then one observes variation in intensity (i.e. loudness) of sound in different locations on the other side of the wall. This variation arises because any sound wave emitted by you generates two waves beyond the wall starting from the two windows. The crests and troughs of these two will add at some places and subtract at other places leading to either an increase or a decrease in the intensity of sound. This phenomenon is called *interference* and is an important characteristic feature of waves (Fig. 1.2). If only one window were open, no interference will be observed since there is now only one set of crests and troughs

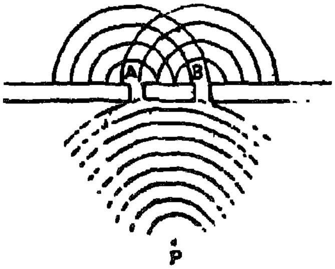


Fig. 1.2 Interference of waves (originating from point P). Each wave generates two-waves beyond the two openings, A and B. Because of phase difference interference takes place.

on the other side of the wall. Thus, in the case of waves, it very much matters whether one or both windows are open when the waves reach them. The observed effects are different in the two cases If there be two or more persons beyond the wall listening to you with one window open, they will all hear you. The fact that one of them has "caught" your sound does not prevent some one else from "catching" the same sound at the same time All the wave effects we have described are due to their delocalized nature.

Let us now see why electrons are regarded as having a dual nature An electron beam can show interference effects (you have studied this in Part I of your Physics book). Interference being a characteristic property of waves, electrons in motion are assigned a wave-like behaviour When an individual electron strikes a zinc sulphide screen, it produces a spot of light known as a *scintillation* Each striking electron produces just one scintillation point. The scintillation and, therefore, the striking electron is localized and not spread out on an area like a wave. This suggests that electrons in motion exhibit a particle-like behaviour too Thus, electrons show a dual nature. A light beam shows interference phenomenon (*see* Physics Book, Part I), thus establishing its wave nature The particle nature of light is evident indirectly in the *photoelectric effect.* We shall describe here the main features of the photoelectric effect.

When a beam of light falls on a metal like caesium, electrons are ejected from it. It is observed that the kinetic energies of emitted electrons are proportional to the frequency of light used but are independent of intensity of such light. Increasing intensity increases the number of ejected electrons but does not affect their kinetic energies. These observations are inexplicable on the basis of wave nature of light. The energy of a wave is related to its amplitude and, hence, to its intensity. One would, therefore, expect that a more intense beam incident at a spot should expel electrons with higher kinetic energies. However, the energy of ejected *photoelectrons* is proportional only to the frequency of light This suggests that light should be treated as consisting of particles. These particles of light are called *photons.* The energy (E) of each photon is proportional to the frequency (ν) of light, i.e. $E = h\nu$, h being a constant of proportionality called Planck's constant.

The photoelectric effect is now easy to explain When a higher frequency light is used, it is equivalent to using photons of higher energy. The ejected electrons would, thus, possess more energy per electron as is observed. Increasing the intensity (keeping frequency fixed) means increasing the number of photons. This results in ejection of photoelectrons in larger numbers but does not affect their energies. The photoelectric effect, thus, forces us to ascribe a particle character to light also. In short, light must also be regarded as having a dual nature:

1.2 de BROGLIE EQUATION

If an electron has a wave character, it should also have a wavelength. The French scientist, Louis de Broglie, deduced in 1923 a relationship between wavelength (λ)

of an electron in motion and its velocity, *v*, or momentum, *p*. This relationship is given by the equation

$$\lambda = \frac{h}{mv} = \frac{h}{p} \qquad \text{......(1.1)}$$

where *m* is the mass of an electron and *h* is the Planck's constant. This relationship has been fully verified by experiment. The de Broglie equation can thus be used to calculate the wavelength of a moving electron if its velocity is known.

Example 1.1

A moving electron has 4.55×10^{-25} joule of kinetic energy. Calculate its wavelength

Solution

The kinetic energy of the electron is given by:

$\frac{1}{2}mv^2 = 4.55 \times 10^{-25}$ joule

$$\text{Therefore,} \quad v^2 = \frac{9.1 \times 10^{-25}}{m}$$

The mass (*m*) of an electron is 9.1×10^{-31} kg. The value of erg in CGS units is g cm^2 sec^{-2}. Substituting these values in the above equation, we get

$$v^2 = \frac{9.1 \times 10^{-25}}{9.1 \times 10^{-31}} = 10^6 \text{ m}^2/\text{sec}^2$$

$$v = (10^6)^{\frac{1}{2}} \quad 10^3 \text{ m sec}$$

From de Broglie equation and Planck's constant value of 6.6×10^{-34} joule sec or kg m^{2}sec^{-2}. sec, we have

$$\lambda = \frac{h}{mv} = \frac{6.6 \times 10^{-34}}{9.1 \times 10^{-31} \times 10^3} \cdot \frac{\text{kg m}^2 \text{ sec}^{-2} \times \text{sec}}{\text{kg} \times \text{m sec}^{-1}}$$
$$= 7.2 \times 10^{-7}\text{m}$$

The de Broglie equation applies not only to electrons but also to other material objects in motion, e.g. neutrons, protons, atoms, molecules, etc. The equation shows that λ decreases as *m* or *v* or both increase. The wavelengths of moving objects like a cricket ball in flight, a fast moving car, etc., are very small on account of their extremely large masses The wave character of bodies which we come across in everyday life is, therefore, neither apparent nor of any consequence.

1.3 THE UNCERTAINTY PRINCIPLE

Moving objects as we see around us all move along definite paths or ***trajectories***. Whether it is a ball thrown or a car going from one place to another, or planets moving around in the sky, all these bodies trace definite trajectories. The trajectory of an object is determined by its initial position and velocity (including speed and direction) at various moments. Thus, if we know where a body is at a particular instant and if we also know its velocity at that instant, we can tell where the body would be sometime later. Hence, we say that the initial position of an object and its velocity at various times fix its trajectory. For a subatomic object like an electron, however, it is impossible to simultaneously determine its position and velocity at any given instant to an arbitrary degree of precision Consequently, it is not possible to talk of the trajectory of an electron The impossibility of simultaneous determination of position and velocity of small particles in motion was first deduced by Werner Heisenberg in 1927 as a direct consequence of the dual nature of light and matter. This principle is known as *Heisenberg's uncertainty principle.*

To understand this principle, consider the problem of determining the position of an electron. To see an electron we have to use light. If we use light of wavelength λ to locate the electron, we know from the principles of optics that the position of electron cannot be located more accurately than $\pm\lambda$. It follows that one can locate the electron as accurately as one desires by choosing a light of appropriately small wavelength. However, light too has a dual nature. From a particle point of view, observing an electron requires the collision of at least one photon with the electron. According to the de Broglie equation, light of a wavelength λ corresponds to photons having a momentum, $p=mv=h/\lambda$. If we choose a small value for λ to determine the position of the electron precisely, the momentum of the photon becomes large and an unknown part of this momentum is transferred to the electron at the time of collision This changes the velocity of the electron by an unknown amount It would seem that we can minimize this disturbance by choosing photons with small values of p. But the de Broglie relation shows that λ will now be large, leading to imprecise determination of position as it cannot be determined to a greater precision than $\pm\lambda$. A more detailed analysis of this situation has shown that if the uncertainties (i e. imprecision) in position and in momentum of an object are Δx and Δp respectively, then the product of these can never be smaller than the Planck's constant, h, divided by 4π. This fact can be expressed in the following form :

$$\Delta x \times \Delta p \geqslant \frac{h}{4\pi}$$

The sign $\geqslant$, means that the product of Δx and Δp can be either greater than or equal to but never smaller than $h/4\pi$. If Δx is made small, Δp increases and vice versa. Since Δp is equal to $m\Delta v$, the above equation is equivalent to saying that position and velocity cannot be simultaneously determined to an arbitrary precision as stated in the beginning of this section.

The uncertainty principle is one of the basic principles of modern science. You may wonder that since this principle rules out existence of definite trajectories, how is it that we continue to talk of paths of balls, cars, planets, etc. ? The answer to this question is that the effect of the uncertainty principle is important only for the motion of sub-microscopic objects and is negligible for that of large objects. This point is shown by the following examples.

Example 1.2

Calculate the uncertainty in velocity (Δv) of an electron, if the uncertainty in its position (Δx) is of the order of 1 Å (i.e. 10^{-10}m)

Solution

From Heisenberg's uncertainty principle.

$$\Delta x \cdot \Delta p = \Delta x \; m\Delta v = \frac{h}{4\pi}$$

$$\Delta v = \frac{h}{4\pi \; \Delta x . m}$$

$$= \frac{6.6\times10^{-34}}{4\times\frac{22}{7}\times10^{-10}\times9.1\times10^{-31}} \; \frac{\text{kg m}^2\ \text{sec}^{-2}\times\text{sec}}{\text{m.kg}}$$

$$= 5.7\times10^{5}\ \text{m/sec}$$

If the velocity of electron becomes uncertain by this huge amount, there is hardly any point in talking about its precise velocity Consequently, talking about the trajectory of an electron makes no sense

Example 1.3

Calculate the uncertainty (Δv) in velocity of a cricket ball (mass = 0.15 kg), if the uncertainty (Δx) in its position is of the order of 1 Å (i.e 10^{-10}m)

Solution

Following the solution of Example 1.2, we can write

$$\Delta v = \frac{6.6\times10^{-34}}{4\times\frac{22}{7}\times10^{-10}\times0.15} \; \frac{\text{kg m}^2\ \text{sec}^{-2}\times\text{sec}}{\text{m}\times\text{kg}}$$

$$= 3.5\times10^{-28}\ \text{m/sec}$$

Compared to the usual velocity of a cricket ball, this uncertainty is negligible We can, thus, talk about the simultaneous position and velocity of a cricket ball at any moment The concept of a trajectory makes sense in this case

1.4 ORBITALS AND QUANTUM NUMBERS

Newton first formulated the *laws of motion* These laws make up *Newtonian mechanics*. They are successful in describing the motion of large bodies However, they fail for the motions of an electron since a moving electron shows a dual character and, therefore, cannot be treated as a "pure" particle The theory, which allows for the dual nature of a moving particle was developed in 1925 by three physicists, Werner Heisenberg, Erwin Schrodinger and Paul Dirac. This theory is called *quantum mechanics*. It seems to be in complete agreement with the experimental information about the structure of atoms and molecules. Quantum mechanics cannot be presented in a brief and elementary manner. So, we shall not attempt here to state its laws, Instead, we shall describe only some of the results, which are useful in understanding chemical behaviour in terms of electronic structures of atoms and molecules.

The motion of an electron around the nucleus cannot be described in terms of *orbits*. An orbit means a definite trajectory for the electron, and the concept of such a trajectory is incorrect according to the uncertainty principle. The motion of electrons about a nucleus is described in quantum mechanics by a set of mathematical expressions required by the allowed quantized energy states of the electron. These expressions are called *orbital wave functions* or more commonly, just *orbitals*. The individual wave functions are denoted by the symbol ψ (pronounced as *sy* rhyming with *my*).

In a physical sense, the orbital of an electron is a part of space around the nucleus in which the particular electron spends most of its time and has a high probability of being found.

Electronic orbitals in atoms are called *atomic orbitals*, while those in a molecule are called *molecular orbitals*. It turns out that for a particular orbital, the electron has fixed energy. This is true whether we are considering an electron in an atom or in a molecule. For an atom, it also happens that the *angular momentum* of an electron is fixed. The atomic orbitals can thus be specified by giving the corresponding energies and angular momenta. These energies and angular momenta, however, do not vary continuously from one orbital to another; both of them are quantized. The quantized values can be expressed in terms of the so-called *quantum numbers*, which are denoted by *n* and can have any positive integral value except zero (e.g. 1,2, 3, .etc.). These quantum numbers tell us about energies and angular momenta of electrons on one hand, while on the other they can be used to label the orbitals. To understand these points better, let us consider the hydrogen atom, which is the simplest of all atoms.

It can be shown that the electron in an hydrogen atom can have only the quantized energy values according to the expression (*see* Physics Book, Part I) :

$$E = -\frac{2\pi^2 me^4}{h^2} \cdot \frac{1}{n^2} \qquad \ldots\ldots\ldots (1.3)$$

where *m* is the mass of electron, *e* its charge, *h* the Planck's constant, and *n* the quantum number. The energy, *E*, in Eq. 1.3 is actually that of the electron-proton pair, though it is generally spoken of as energy of the electron. If an electron is sufficiently far from a proton so that there is no interaction between them, the electron energy can be taken as zero. Compared to this situation, the energy of the electron in an hydrogen atom given by the above formula is negative or less than zero. The negative sign for energy indicates that the pairing of electron and proton in the atom is stabilized.

According to Eq. 1.3 the largest negative value of energy (i.e. maximum stability) is obtained when *n* has the smallest permitted value, which is 1. Thus, $n=1$ gives the lowest energy state of the electron in hydrogen atoms. This state is called the *ground state* of the electron or of the atom. If the known values of *m*, *e* and *h* are substituted in Eq. 1.3, the energy of the ground state works out to -1.312×10^6 J mol^{-1}. What will happen if 1.312×10^6 J mol^{-1} of energy is given to the hydrogen atom ? The energy per mole of atoms for the system will become zero, i.e. the electrons will be far removed from the protons. This situation is described as *ionization* of hydrogen. Hence, *ionization energy* of hydrogen, which is the energy needed to remove the electron in the atom away from the influence of its proton, is $+1.312 \times 10^6$ J mol^{-1} for hydrogen atoms. This has been confirmed by experiment. Note the positive sign for ionization energy. The positive sign means that this energy is added to the hydrogen atoms, i.e. the energy is supplied from outside. Let us now calculate the electron energy for the quantum number n equal to 2. The formula shows that this is $-1.312 \times 10^6/4$ J mol^{-1} or -3.28×10^5J mol^{-1}. This reduced negative value indicates that in this state the atom is less stable compared to the ground state. This will be true also for all the other higher values of n.

All states with n values greater than 1, are called *excited states* of hydrogen atom. They can be obtained from the ground state by providing appropriate energies called the *excitation energies* of these states. For example, if $13.12 \times 10^5 - 3.28 \times 10^5 = +9.84 \times 10^5$ J mol^{-1} is provided to hydrogen atoms in the ground state, the electron in the atoms will make a transition from the $n = 1$ to the $n = 2$ state. The various energy states of the electron in an atom are commonly called its energy levels. The meaning of the statement that energy of the electron in the hydrogen atom is quantized would be clear from the energy level formula for the latter. The electron in this atom can have energy equal to either -13.12×10^5 J mol^{-1} ($n = 1$) or -3.28×10^5 J mol^{-1} ($n = 2$), or -1.46×10^5 J mol^{-1} ($n = 3$) and so on, and no energy values in between. Energy quantization is observed in all atomic and molecular systems. However, expressions for energy levels in multi-electron atoms and in molecules are not known as precisely as in the case of hydrogen atom.

In Eq. 1.3, all the factors on the right hand side other than n are constants. Therefore, we may rewrite this equation as :

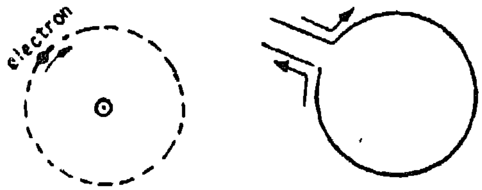
$$E = -\frac{C}{n^2} \qquad \text{.........}(1.4)$$

$$\text{Where } C = \frac{2\pi^2\, me^4}{h^2} \qquad \text{.. .. ..}(1.5)$$

The value of C works out to be 1.312×10^6 J mol^{-1}. The only variable n of Eq. 1.3 or Eq. 1.4 can have positive integral values as stated earlier It is clear that for every given value of n, the energy term in Eq. 1.3 gets a fixed value. For example, if we are told that the electron in a hydrogen atom is in $n = 10$ energy level, we at once know that its energy must be -1.312×10^4 J mol^{-1}. The quantum number n, which specifies values of energy for the electron is called its *principal quantum number*.

It was stated earlier that the electron in a hydrogen atom has angular momentum which is also quantized It should be hardly surprising to know that the quantized values of angular momentum can be specified in terms of another quantum number, denoted by l, and called the *angular momentum quantum number*. The permitted values of l are again positive and integral. They are 0, 1, 2, etc. up to (n-1). Two points should be noted in respect of l. First, l, unlike n, can have a value of zero also. Secondly, whereas n value can be any integer up to infinity, the integral values of l are determined by the value for n and go up to only n-1 Thus, if $n = 6$, l can be only 0, 1, 2, 3, 4 and 5. No other integral values beyond 5 are permitted so long as n has a value of 6. You may wonder, why the l values are restricted by n. The reason for this is quite simple. Existence of angular momentum implies existence of angular kinetic energy for the electron. This obviously can never exceed its total energy as defined by n Therefore, it is understandable that n (which determines total energy) should in some way restrict l (which determines energy linked with angular momentum).

An electron having an angular momentum and, thus, revolving round the atomic nucleus behaves in some ways like an electric current circulating in a wire loop (Fig 1 3). Consequently, it produces a magnetic field which can be observed. The observed magnetism shows quantized nature and this is described by a third quantum number called the *magnetic quantum number* m_l. Since this magnetism is due to the angular momentum, it is expected that values of m_l would depend on the value of l. It is found that for every given value of l, there are $2l+1$ permitted integral values of m_l which range from $-l$ to $+l$, including zero. For instance if $l = 3$, then $2l+1$ or 7 possible values for m_l are -3, -2, -1, 0, $+1$, $+2$ and $+3$.



Current due to a revolving electron

Current in a wire loop

Fig. 1.3 Movement of an electron generates electric current

Apart from the magnetic effect due to its angular momentum (which in turn varies according to the value for l), it is found that the electron has another inherent magnetic property because of spin around its own axis. This effect is quantized according to the spin direction, being clockwise or anticlockwise. This situation leads to a fourth quantum number called the ***spin quantum number***, m_s, which has two permitted values : $+\frac{1}{2}$ and $-\frac{1}{2}$

To summarize, the motion of an electron in an atom is determined by four quantum numbers n, l, m_l and m_s. The restrictions on these are .

$n = 1,2,3,$ . .... .up to ∞ (only positive integers)

$l = 0,1,2,..$ ...... .up to (n-1) (zero and positive integers only)

$m_l = -l, (-l+1), .., 0, ..., (l-1), l;$ ($2l+1$ values in all)

$m_s = +\frac{1}{2}$ or $-\frac{1}{2}$ (only two values)

The electronic energy levels in hydrogen atom are given in terms of the principal quantum number n only, but energy levels in all the other atoms (which contains more than one electron) are determined by n and l together. We shall discuss the dependence of energy levels in multi-electron atoms on n and l in somewhat greater detail shortly as it has important consequences on the form of the Periodic Table.

Each permitted combination of n, l and m_l defines some possible energy state of electron in the atom. The wave function or the orbital corresponding to this state may, therefore, be labelled by these three quantum numbers. The value of n is given first It is followed by the letters s, p, d or f, which respectively signify $l=0$, $l=1$, $l=2$ and $l=3$ values The three possible m_l values for $l=1$ (i.e. p orbitals) are labelled as p_x, p_y and p_z. For $l=2$ (i e. d orbitals), the five possibilities for m_l are indicated as d_{z^2}, $d_{x^2-y^2}$, d_{xy}, d_{xz}, and d_{yz} The significance of these subscripts can be fully explained only in a more advanced course. Each of the orbitals can accommodate two electrons which must have spin quantum numbers of opposite sign. This requirement arises from the *Pauli's exclusion principle* which states that no two electrons in an atom can have the same set of four quantum numbers

1.5 SHAPES OF ORBITALS

On the basis of the wave mechanical treatment of motion of an electron around a nucleus we can calculate for a particular orbital wave function the probability of an electron being found at various distances from the nucleus and in various directions. This procedure shows that the radial electron probability* for an 1s orbital *spherically symmetrical* (Fig. 1·4a). For the hydrogen atom the radial electron probability for 1s orbital has a maximum value at 0 53Å from the nucleus and rapidly decreases for distances less than and more than 0 53Å.. The radial electron probability for 2s, and all other s orbitals is also spherically symmetrical (Fig. 1·4b).

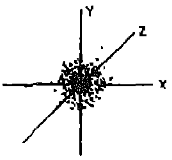


Fig. 1 4 (a) A 1s orbital

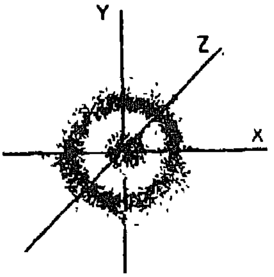


Fig. 1.4 (b) A 2s orbital.

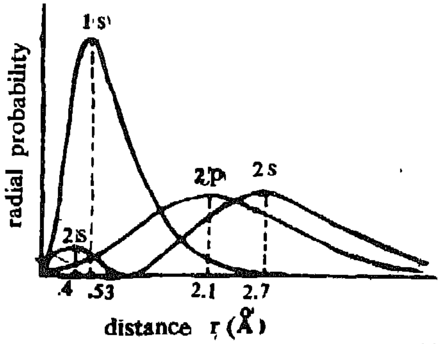


Fig. 1 5 A curve showing radical probabili vs. distance from nucleus.

Following points should be noted about radial electron probability in respect of s orbitals:

(i) The number of probability peaks in the radial probability distance-from-nucleus curves for any s orbital is equal to the related principal quantum number n; one for *1s*, two for *2s* orbital and so on (Fig. 1.5).

(ii) For s orbitals with multiple probability peaks, the peak heights increase as their distances from the nucleus increase. Thus for the *2s* orbital in an hydrogen atom a smaller peak occurs at 0.4 Å and a larger peak occurs at 2.7 Å. A smaller peak height means a lesser probability also.

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* Radial electron probability is the product of electron probability at a certain distance from the nucleus and the surface area sphere of the same radius.

(iii) A larger distance from the nucleus of the higher peak for the 2*s* orbital indicates a larger size of the 2*s* orbital. It should however be remembered that there is some probability for the electron to be at the distance of the smaller peak, howsoever small this probability may be.

Radial electron probability distribution patterns for any of the 2*p* orbitals do not show spherical symmetry. It takes the form of a dumbell *along* a coordinate axis (Fig 1.6)

The three 2*p* orbitals have the same pattern of radial electron probability (they have thus the same shapes), but they have different directional dependence and hence lie along the different coordinate axis.

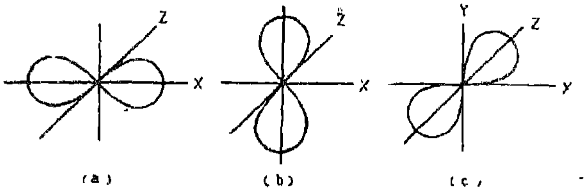


Fig 1.6 The 2p orbitals—(a), (b) and (c) denote p_x, p_y and p_z orbitals respectively

The radial electron probability for a 2*p* orbital shows only one peak. This is at 2.1 A from the nucleus in hydrogen atom. Thus, the electron in 2*p* orbital will be essentially outside the 1*s* orbital (Figure 1.5) Likewise the electron in 2*s* orbital will also be outside the 1*s* and the 2*p* orbitals. Yet electron in 2s orbital has added probability for being at the inner peak of 1*s* orbital at 0.4 Å. In case of one electron atoms like hydrogen, the energy of the electron is determined by only the principal quantum number, *n*. But for a multi-electron atom as lithium (Z=3), the electron energy is determined both by its principal quantum number *n* and the orbital quantum number *l*. A 2*s* electron experiences the attraction of the full nuclear charge of 3 units, when it is at a closer distance to the nucleus than the electron in 1*s* orbital. However, when the 2*s* electron is outside the 1*s* orbital, two units of nuclear charge are screened from it by the two electrons in the 1*s* orbital. In case of the 2*p* orbital, the electron being essentially outside 1*s* orbital, it will experience the attraction of only screened nuclear charge Thus, relatively speaking, in a multi-electron atom a 2*p* electron is bound to the nucleus somewhat less firmly than a 2*s* electron. This also means that the energy of a 2*s* electron is less than that of a 2*p* electron. This accounts for the third electron in *Li* entering the

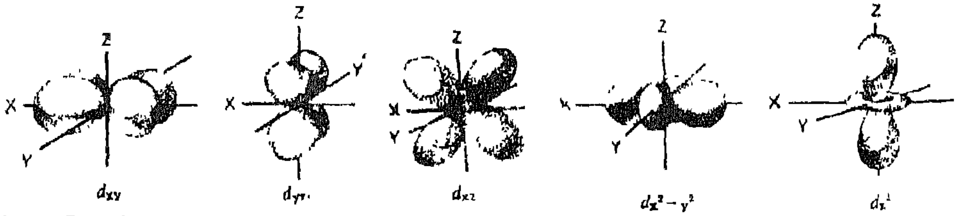


Fig. 1.7 Directional dependence of the probability of an electron in the five 3rd orbitals. (Dots are used only to show three dimensional burdents of the orbitals).

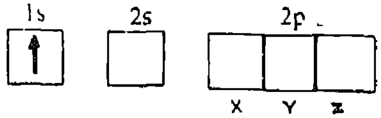
2s rather than the *2p* orbital. By the same argument an electron will have a lower energy in the 3 *s* orbital than in the *3p* orbital and an electron will enter the 3 *s* orbital before the 3p orbital.

1.6 ELECTRONIC CONFIGURATION OF ATOMS

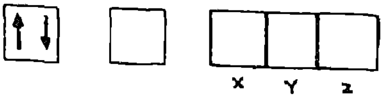
You are already familiar with the use of the Aufbau principle to write the electronic configuaration of atoms (Section 2.5 of Part I) Since we have discussed the various orbitals in greater detail now, we shall reconsider this topic pointing out some additional features

It will be convenient to indicate orbitals by squares as we had done in Unit 4 of Part I. An empty square will mean an unoccupied orbital. A single electron in an orbital will be shown by drawing one arrow in a square and a pair of electrons will be shown by a pair of arrows with heads in reverse directions. The arrowhead (i.e ↑ or ↓) will signify the 'up' or 'down' orientation of the electron spin. For energy sequence of orbitals, we shall use Fig. 1.8. The configuration of orbitals, H($1s^1$), He ($1s^2$), Li ($1s^22s^1$) and Be ($1s^22s^2$) can be shown as follows :

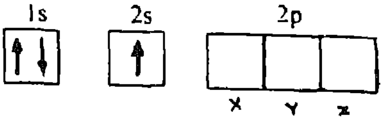
H $1s^1$



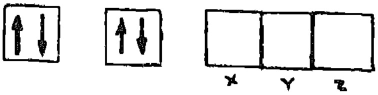
He $1s^2$



Li $1s^22s^1$

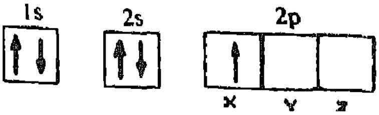


Be $1s^22s^2$



The fifth electron for boron atom can be placed in any one of the three (equal energy or degenerate) *2p* orbitals with either up or down orientation. Let us place it in $2p_x$ with up orientation.

B $1s^22s^22p_x^1$



A new feature arises with the atom of the next element, namely, carbon. Where should we place the sixth electron ? If we put it in $2p_x$, there will be a pair of electrons

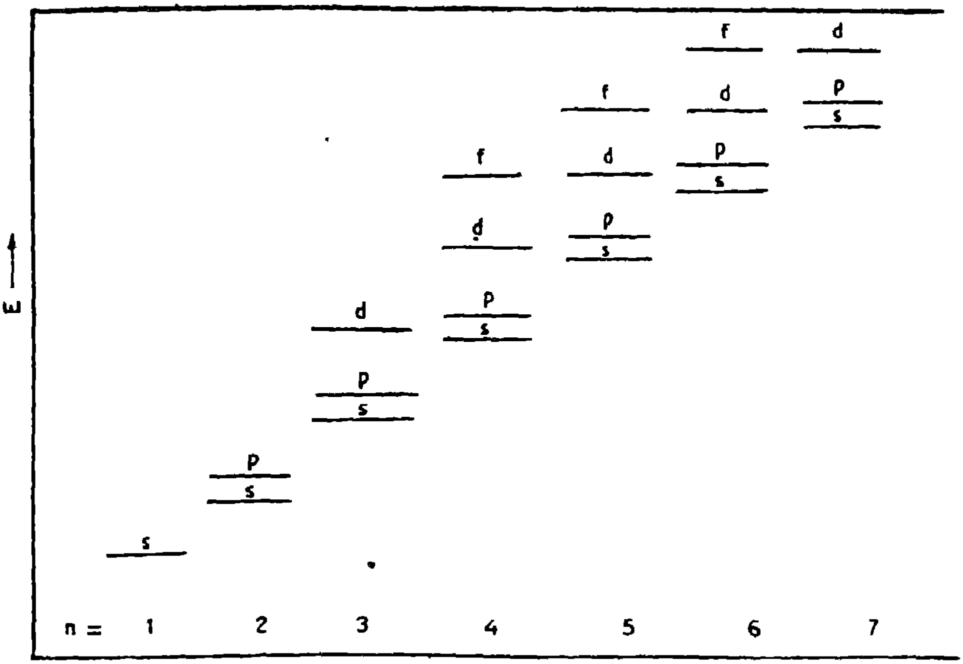
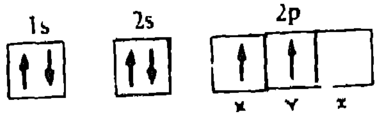


Fig. 1.8 Relative energies of various orbitals in atoms.

occupying the same region of space but if we put it in either $2p_y$ or $2p_z$, the two electrons will be occupying different regions of space. (This follows from Fig. 1.6 which shows that p_x, p_y and p_z are along three different directions in space.) Since electrons repel each other, it is obviously better for stability that they enter in different and more distant orbitals to reduce repulsions between them. We shall, therefore, place the sixth electron in the $2p_y$ orbital. What about the orientation of spin? It may appear that it does not matter whether the sixth arrow is up or down. However, for reasons which cannot be explained at this stage, the parallel arrangement of spins gives a lower energy for the atom than when the spins are anti-parallel. This means that the electron arrow in the $2p_y$ orbital must have an up orientation (which is parallel to the $2p_x$ electron orientation). Thus, the carbon atom configuration becomes:

C $1s^2 2s^2 2p^2$



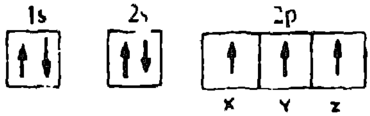
We state at this stage two rules, known as Hund's rules, which are useful for dealing with the type of situation met with in the carbon atom

(i) When a group of empty orbitals having equal energies is available (like $2p_x$, $2p_y$ and $2p_z$ above), the electrons should first be allotted singly to different orbitals (The basis of this rule is that such an allottment reduces the force of repulsion and, hence, corresponds to a lower energy configuration).

(ii) When electrons are placed in different equal-energy orbitals, their spins should be parallel. (The basis of this rule lies in the magnetic effects of electron spin).

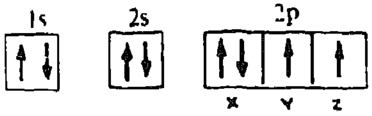
The use of these two rules shows that the nitrogen atom configuration will be

N $1s^2 2s^2 2p^3$



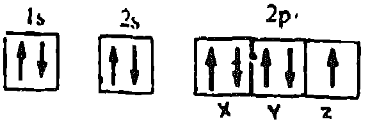
The next electron has to be placed in one of the singly occupied $2p$ orbitals since the next orbital, $3s$, is much higher in energy. Moreover, Pauli principle demands that for going into an already half-filled orbital an electron must have a spin opposite to that of the electron already there. Consequently, configuration of oxygen atom is :

O $1s^2 2s^2 2p^4$

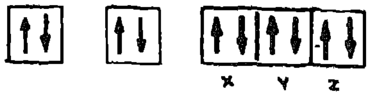


Similar reasoning yields the following further electronic configurations :

F $1s^2 2s^2 2p^5$



Ne $1s^2 2s^2 2p^6$

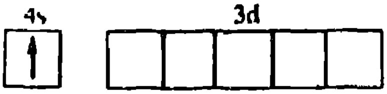


The K and L energy shells ($n = 1$ and $n = 2$) have become fully occupied in reaching neon. The additional electrons are, therefore, assigned to the M energy shell beginning with sodium. The configurations of elements from sodium to argon is given on page 15. They are derived in exactly the same manner as the configurations of elements lithium to neon given above. Only the valence or M shell orbitals are shown. It is understood that the first ten electrons in each element are distributed in K and L shells as described for neon.

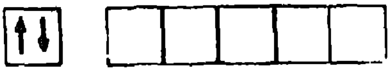
		3s	3p		
			x	y	z
Na	$3s^1$	↑			
Mg	$3s^2$	↑↓			
Al	$3s^2 3p^1$	↑↓	↑		
Si	$3s^2 3p^2$	↑↓	↑	↑	
P	$3s^2 3p^3$	↑↓	↑	↑	↑
S	$3s^2 3p^4$	↑↓	↑↓	↑	↑
Cl	$3s^2 3p^5$	↑↓	↑↓	↑↓	↑
Ar	$3s^2 3p^6$	↑↓	↑↓	↑↓	↑↓

In potassium and calcium, the 4*s* orbital is occupied first as it is lower in energy than the 3*d* orbital.

K $4s^1$

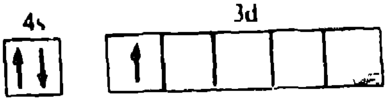


Ca $4s^2$

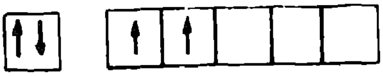


To proceed further, we need one more rule. It is observed that when the set of $5d$ orbitals are either half-full or completely full, some extra stability results. This means that configuration d^5 and d^{10} are additionally preferred. Let us now return to the elements beyond calcium where the $3d$ orbital is getting filled. The next three elements are .

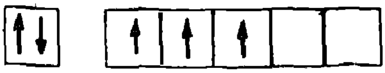
Sc $4s^2 3d^1$



Ti $4s^2 3d^2$

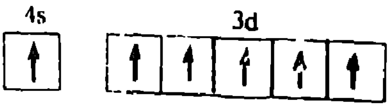


V $4s^2 3d^3$



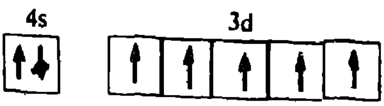
The element Cr which follows V does not, however, have the configuration $4s^2 3d^4$ instead, it has the configuration $4s^1 3d^5$. This happens because d^5 has extra stability as mentioned above and, therefore, the configuration $4s^2 3d^4$ rearranges to give the lower energy arrangement, $4s^1 3d^5$. Thus, chromium is written as :

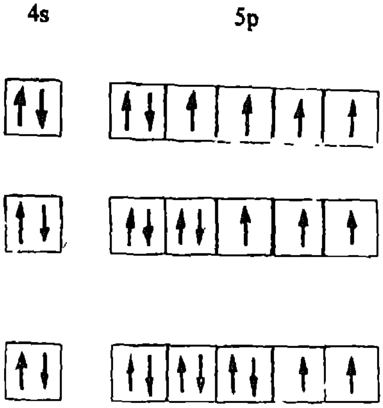
Cr $4s^1 3d^5$



followed by.

Mn $4s^2 3d^5$



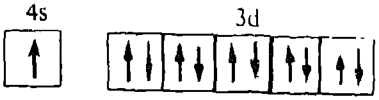


Fe $4s^23d^6$

Co $4s^23d^7$

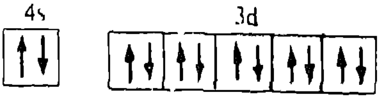
Ni $4s^23d^8$

The extra stability of d^{10} results in the next element copper having the configuration $4s^13d^{10}$ rather than $4s^23d^9$.



Cu $4s^13d^{10}$

This is followed by :



Zn $4s^23d^{10}$

The distribution of electrons in different orbitals for the remaining elements can be worked out in exactly the same manner as no new principles are required

EXERCISES

1.1 State the de Broglie relation between the wavelength and momentum of a particle.

1.2 Calculate the momentum of a particle which has a de Broglie wavelength of 1A

1.3 Calculate and compare the energies of two radiations, one with a wavelength of 8000A and the other with 4000A.

1.4 What do you understand by an atomic orbital ? What are the shapes of the s, p and d orbitals.

1.5 What do you understand by quantum numbers ? What is the significance of these quantum numbers ?

1.6 What are the n, l and m_l values for $2p_x$ and $3p_z$ electrons ?

1.7 Write and explain in brief
- (i) Aufbau principle
- (ii) Pauli's exclusion principle
- (iii) Heisenberg's uncertainty principle

1.8 In an atom, the first shell may contain up to 2 electrons, the second shell up to 8, the third shell up to 18, and the fourth shell up to 32 electrons. Explain this arrangement in terms of quantum numbers.

1.9 Write the sequence in which electrons fill in the various energy levels in an atom.

1.10 State Pauli's exclusion principle and Hund's rule. What is the importance of these rules in filling the electrons in various energy levels ?

1.11 Write the electronic configurations of elements of atomic numbers 10, 17, 25, 29 and 37.

1.12 Explain why half-filled and completely filled orbitals have extra stability.

1.13 What designation are given to orbitals having : (i) $n=2$, $l=1$; (ii) $n=2$, $l=0$; (iii) $n=4$, $l=3$; (iv) $n=4$, $l=2$; and (v) $n=4$, $l=1$?

1.14 Write down the different relationships between :

   (i) Wave number and wavelength
   (ii) Wave frequency and wavelength
   (iii) Wave frequency and momentum

1.15 What atoms are indicated by the following configurations ? Are they in the ground or excited state?

   (i) $1s^2\ 2s^2\ 2p_x^2\ 2p_y^2\ 2p_z^1$
   (ii) $[\mathrm{Ar}]\ 4s^2\ 3d^5$
   (iii) $1s^2\ 2s^1\ 2p_x^1\ 2p_y^1\ 2p_z^1$

UNIT 2

More About Molecules

Unit 4 of Part I dealt with chemical bonds and molecules. You will recall that a group of atoms remaining together as a stable combination and having characteristic properties of its own is called a molecule. Such a combination is stable because it has a lower energy compared to the constituent atoms existing separately. It is convenient to think that atoms in a molecule are linked by chemical bonds. There exist several types of bonds such as covalent bond, ionic bond, hydrogen bond and some others. Two chemically bonded atoms have a definite distance of separation (*bond length*) and a definite *bond energy*. (*Bond energy* is the energy released on bond formation). The geometry or shape of molecules depends on the relative arrangement of bonds in space or the *bond angles*. Bond types, bond lengths, bond angles and bond energies between themselves determine the physical and chemical behaviour of molecules. It can be said that understanding chemistry is essentially the understanding of the nature of chemical bonds.

The electronic theory of chemical combinations clearly reveals the nature of chemical bonds. You have already seen in some detail (Section 4.3, Part I) why and how two hydrogen atoms form a hydrogen molecule. In an isolated H atom, the electron is attracted by one nucleus, only in this case it happens to be just a proton. In a H_2 molecule, however, each of the two electrons are attracted by two protons. This additional attraction is responsible for the lowering of energy and, hence, for the stability of H_2 *molecule*. Generally, molecule formation results whenever valence electrons of participating atoms can feel the attractive influence of more than one nucleus. The lowering of energy is maximum for some definite arrangement of atoms for a molecule. Any distortion from this arrangement raises the energy and is, therefore, not favoured. This explains why molecules have characteristic bond lengths and bond angles making a characteristic molecular geometry.

2.1 REVIEW OF VALENCE BOND METHOD

The chemical bond approach was used in Part I of this book to study simple examples of molecule formation. The method discussed there is called the *valence bond* (v.b.)

method Let us consider the H_2 molecule Instead of saying that each electron feels attractive influence of two protons, we can equally well regard that the two protons are sharing a pair of electrons Thus, the chemical bond in hydrogen molecule gets identified with a shared pair of electrons. The mechanism by which such sharing becomes possible is easily understandable The electron in an isolated hydrogen atom is present in the 1s orbital When two such atoms approach each other, this will lead to an overlapping of the atomic orbitals Such an overlap of orbitals permits the two electrons to occupy a common region in space. However, the Pauli principle allows this to happen only if the spins of the two electrons are of opposite kinds We conclude then that the requirements for bond formation are · (i) presence of singly filled orbitals in different atoms, and (ii) the two electrons occupying these separate orbitals having opposite spins.

Under these conditions, an overlap of orbitals can take place leading to a sharing of an electron pair between two nuclei. Application of these ideas to molecules like F_2, H_2O, NH_3, CH_4, C_2H_4, C_2H_2, etc. was covered in Unit 4 of Part I This approach is called v.b method because it directs attention primarily to the role of valence electrons in forming individual chemical bonds. The v b. method was mainly developed by the great American chemist Linus Pauling in about 1930. Pauling was awarded the Nobel Prize in chemistry in 1954

There is another approach to explaining molecular structures. This is known as the *molecular oribital* (m o.) method It was developed mainly by Robert Mulliken, winner of the Nobel Prize in chemistry in 1966 We shall discuss the m.o. approach in the following section.

2 2 MOLECULAR ORBITAL METHOD

The m o description of molecules is very similar to the atomic orbital description of atoms. Just as the electron probability distribution around a nucleus is given by atomic orbitals, the electron probability distribution around a group of nuclei in a molecule is given by m.o. Moleculer orbitals, thus, play the same role in determining the electronic structure of a molecule that atomic orbitals do for electronic structures of atoms In atoms, we tabulate all the atomic orbitals and arrange them in a sequence of increasing energy. The orbitals are labelled by the four quantum numbers n, l, m_1 and m_s We then fill the orbitals one at a time (Aufbau principle), subject to Pauli principle, to arrive at the electronic configuration of any atom. The m o method proceeds in exactly the same way with molecules, and we shall illustrate this by discussing the electronic structure of some simple homonuclear diatomic molecules in which both atoms are identical (i e. H_2, Li_2, Be_2, etc.)

The three steps to be followed are . (i) to tabulate the m o. of homonuclear diatomic molecules, (ii) to arrange them in order of increasing energy, and (iii) to fill them with electrons one at a time, keeping in view the Pauli principle. Step (i) was applied to atoms by considering the possible orbitals of the one-electron atom or the hydrogen atom. It follows that for diatomic molecules, we should similarly consider the possible oribitals of an one-electron diatomic molecule There exists no neutral molecule with a single electron. However, there does exist a positively charged molecular species called molecular hydrogen ion, H_2^+. It can be thought of as a hydrogen molecule from which one of the electrons has been removed H_2^+ ion is not stable enough to be obtained in solutions like other ions It can, however, be produced in discharge tubes Although short-lived, it has been possible to measure many of its properties For example, its bond length is 1 06 × 10^{-10}m (1 06 Å) and bond energy 269 kJ mol^{-1} Being an one-electron molecule, H_2^+ occupies the same place in m.o. treatment that hydrogen atom does in atomic structures

Molecular orbitals of H_2^+ ion: The various m o. of the electron in H_2^+ ion can be deduced by a rather simple reasoning. Consider the lowest energy state (i.e. the ground state) of this molecular ion The m.o. for this state provides probability distribution for the electron in this state. Let us label the two protons in H_2^+ ion as A and B. When the electron is near proton A, we can treat H_2^+ ion as a hydrogen atom plus proton B. Similarly, when the electron is near proton B, the molecular ion can be regarded as a hydrogen atom plus proton A. In the first case, the electron distribution is described by a 1*s* orbital located around A while in the second case it is described by a 1*s* orbital located around B It is reasonable to assume, therefore, that the m o. in this case is made up of two 1*s* atomic orbitals, one centred on A and the other centred on B.

The idea that a m.o can be obtained by combining atomic orbitals located on different nuclei is central to the m.o. method. It is based on the rather obvious expectation that a m o. in the vicinity of a particular nucleus must resemble the atomic orbital around that nucleus. However, there is one feature of this idea which is not so obvious, namely, how are the atomic orbital to be combined together to form new m.o. There are, in fact, two ways of doing it. Thus, when two atomic orbitals are combined, one always gets two m.o. One m.o. is obtained by adding the atomic orbitals and the other by subtracting them. In the former case, it is found that the electron probability in the internuclear region is increased Since this situation favours bonding, the m o. formed by adding atomic orbitals is called a *bonding molecular orbital*. In the second case, the electron probability in the internuclear region is decreased. Since this situation does not favour bonding, the corresponding m.o. is called *antibonding molecular orbital*. As far as energy is concerned, it is obvious that the electron present in the bonding orbital should have a lower energy than the one present in the antibonding orbital

We have seen how the two 1*s* atomic orbitals located on the two protons in H_2^+ ion give rise to a pair of m.o —one bonding and one antibonding. In the same fashion, two 2*s* orbitals located on two protons yield another pair of m.o. Since 2*s* has higher energy than 1*s*, the pair of m o. obtained from the 2*s* orbitals have higher energies than the pair obtained from 1*s*. Within each pair, the bonding orbital, of course, lies lower on the energy scale than the antibonding orbital. Additional pairs of m.o can be obtained from double sets of $2p_x$, $2p_y$, $2p_z$ and other atomic orbitals. The order of energy of 10 m o. arising from two 1*s*, two 2*s*, and six 2*p* atomic orbitals is given in Fig 2.1. The ordering relating to the 2*p* set may look puzzling, but since the explanation is complicated we shall not enter into it at this stage

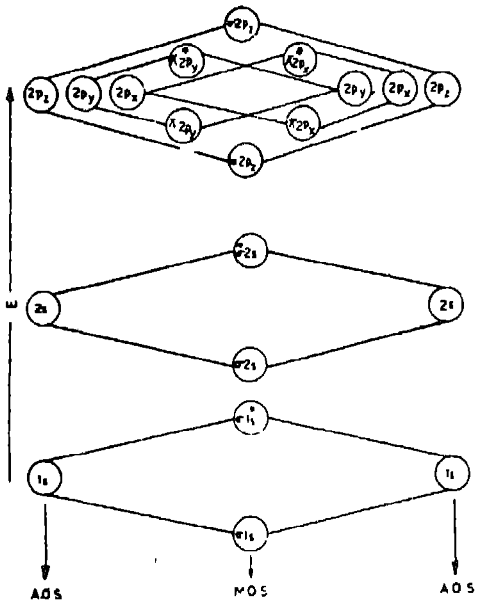


Fig. 2.1 Energy orders for filling molecular orbitals for diatomic homonuclear molecules

In parallel with the *s*, *p*, *d* classification of atomic orbitals, m.o of diatomic molecules are named, σ, π, δ, etc. The meaning of this nomenclature is that the addition and subtraction of two *s* orbitals centred on two nuclei produce m.o. which are symmetrical around the bond axis (Fig. 2.2). Such m.o. are of the sigma (σ) type. If the internuclear axis be regarded as the z-direction, it can be seen that a combination of p_z orbitals of two atoms also produces two σ type m o. (Fig. 2.3). Molecular orbitals obtained in cases of p_y and p_x orbitals are not symmetrical around the bond axis because of the presence of positive lobes above and negative lobes below the molecular plane (Fig. 2.4). Such m.o. are, therefore, not of the σ kind. Molecular orbitals of the type shown in Fig. 2.4 are labelled as pi (π) orbitals. The antibonding orbitals are indicated by putting an asterisk after them. Thus, σ^* and π^* are antibonding σ and π orbitals respectively. Atomic orbitals which are involved in the formation of m.o. are generally given as subscripts For example, σ_{2s} means a bonding m.o. formed by the addition of two 2*s* atomic orbitals and π^*2p_y means an antibonding m o. formed from the two $2p_y$ atomic orbitals.

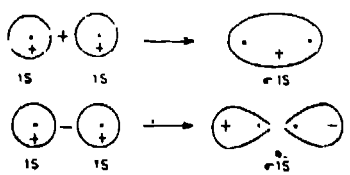


Fig 2.2 Molecular orbitals formed by adding and subtracting two 1*s* atomic orbitals. σ1*s* and σ*1*s* are bonding and antibonding molecular orbitals

We are now in a position to apply the Aufbau principle to derive the electronic configuration of any homonuclear-diatomic molecule. However, before we do so, it is of interest to find the relationship between electronic configuration and molecular behaviour. This is done by using a few simple rules :

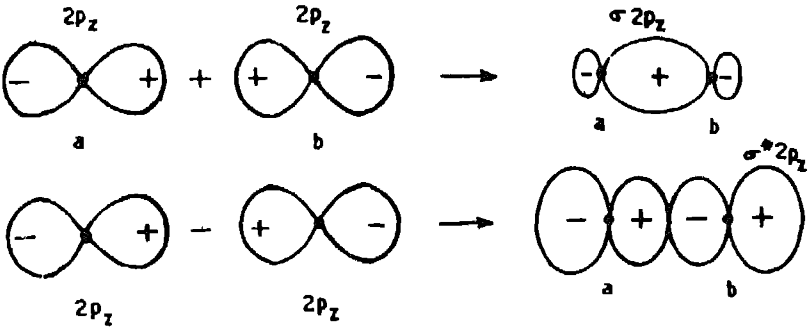


Fig 2.3 Formation of $\sigma 2p_z$ and $\sigma^* 2p_z$ molecular orbitals by combination of $2p_z$ atomic orbitals.

(a) If N_b electrons occupy bonding orbitals and N_a electrons are in antibonding orbitals, (i) the molecule is stable, if N_b is greater than N_a; (ii) the molecule is unstable, if N_b is less than N_a; and (iii) the molecule is unstable, if N_b is equal to N_a.

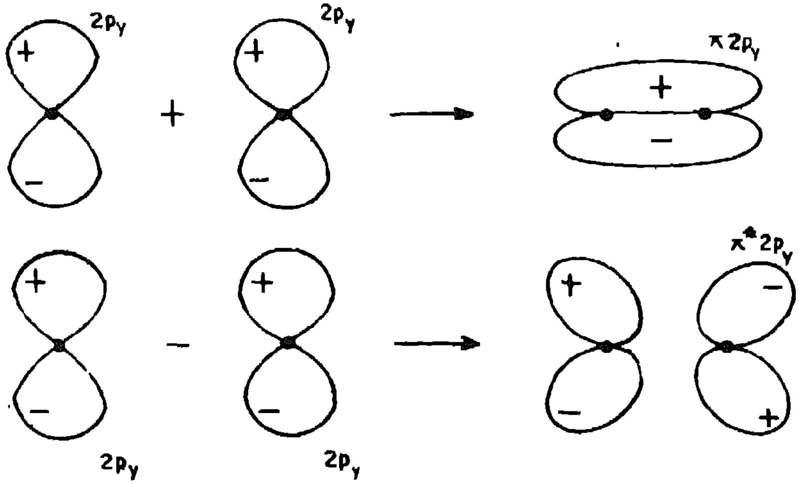


Fig. 2.4 Formation of $\pi 2p_y$ and $\pi^* 2p_y$ molecular orbitals by combination of $2p_y$ atomic orbitals.

Statements (i) and (ii) are easy to understand. In (i), more bonding m.o. are occupied so the bonding influence is stronger and a stable molecule results. In (ii), the reverse is the case and the molecule is unstable. The explanation for (iii) is that the antibonding effect is somewhat stronger than the bonding effect

(b) For estimating relative stability, it is convenient to introduce a quantity called *bond order* (b o.) This is defined as half of the difference between numbers of electrons in bonding and antibonding orbitals, i.e b o = $\frac{1}{2}(N_b - N_a)$ · ·

The rules given in (a) can now be restated as . A negative or zero b.o. means an unstable molecule while a positive b.o. means a stable molecule The stability of a diatomic molecule as measured by its dissociation energy is proportional to its b.o Thus, a molecule with a b.o. of two has greater dissociation energy than a molecule with a b o of one or one and a half

(c) Integral bond orders of one, two or three correspond respectively to what we call single, double or triple bonds The bond order concept in the m o method, thus, corresponds to the familiar concept of a chemical bond The correspondence is, however, not exact because b.o. can be non-integral whereas we normally do not think of fractional chemical bonds.

(d) Bond order is inversely related to bond length.. The higher the b.o. value, shorter is the bond

(e) If all the electrons in molecule of a substance are paired, the substance is diamagnetic; otherwise it is paramagnetic

We shall now apply these ideas to study some of the diatomic molecules of the elements of the first and second rows of the Periodic Table

H_2^+. The only electron in this molecular ion occupies the lowest energy orbital, $\sigma 1s$ This is a bonding m o. The b.o can be calculated as follows .

$$\text{b.o.} = \frac{1}{2}\ (N_b - N_a) = \frac{1}{2}\ (1\text{-}0) = \frac{1}{2}$$

Positive value indicates that the molecular ion has some stability This, of course, also follows from the fact that the lone electron in this ion is in a bonding m o. The existence of unpaired electrons should make the molecule paramagnetic. The stability of the ion as well as its paramagnetism are experimentally observed

H_2. The second electron of this two-electron molecule will also go in the $\sigma 1s$ orbital but with opposite spin. This explains the observed diamagnetism of molecular hydrogen. The bond order is

$$\text{b o} = \frac{1}{2}\ (N_b - N_a) = \frac{1}{2}\ (2\text{-}0) = 1$$

which means that we can think of the two hydrogen atoms as being connected by a single bond The b o value also shows that compared to H_2^+, the bond in H_2 should be stronger and shorter. The experimental value of 433 kJ mol^{-1} for bond energy and of 0.74×10^{-10}m for bond length support our expectation.

He_2^+. The third electron occupies the antibonding orbital σ^*1s The b.o. is $\frac{1}{2}$ (2-1) $= \frac{1}{2}$, i.e. same as in H_2^+. The dissociation energy and bond length should be comparable to those of H_2^+. The molecule should be paramagnetic. All these conclusions are in agreement with experiment

He_2. The fourth electron also goes into σ^*1s orbital making the b.o. zero. No such molecule should be formed nor has it been observed. We can proceed in the same fashion to the homonuclear, diatomic molecules formed by Li, Be, B, and C. However, the molecules Li_2, Be_2, B_2, and C_2 are not of any interest from a chemist's point of view We shall, therefore, omit their discussion and, instead, consider the diatomic molecules formed by nitrogen, oxygen and fluorine which are chemically important.

N_2: This molecule has 14 electrons. These have to be accommodated in the seven lowest energy orbitals which, according to the energy level diagram, are . $\sigma 1s$, σ 1s, $\sigma 2s$, σ^*2s, $\sigma 2p_z$, $\pi 2p_x$, and $\pi 2p_y$ The 5 bonding orbitals have 10 and the two antibonding ones have 4 electrons. Therefore, the b o is .

$$\tfrac{1}{2}\,(N_b-N_a)=\tfrac{1}{2}\,(10-4)=3$$

which agrees with the traditional view that N_2 *contains* a triple bond The b o. also suggests that dissociation energy should be high. The experimental value of 945.0 kJ mol^{-1}—the highest amongst the diatomic molecules—supports the expectation Since all the electrons are paired, the observed diamagnetism is also understandable

O_2: Fourteen of the 16 electrons in this molecule will be distributed as in N_2 The energy level diagram shows that after 14 electrons have been alloted, there are two vacant orbitals π^*2p_y and π^*2p_x with the same energy From Hund's rules, it follows that the two remaining electrons should be assigned one each to π^*2p_y and π^*2p_x with their spins parallel. In this distribution, there are 10 bonding electrons (as in N_2) but 6 antibonding electrons. The b.o , therefore, becomes 2 which accounts for the double bond known to be present in O_2 molecule The two unpaired spins should make oxygen *paramagnetic*. It is actually observed to be so You will recall that the simple valence bond approach wrongly predicted O_2 to be diamagnetic (*see* p 52, Part I). We now see how the m o. approach successfully tackles this question.

F_2: The two additional electrons beyond O_2 (F_2 has 18 while O_2 has 16 electrons), go into the half-filled π^*2p_y and π^*2p_x orbitals. F_2 has, thus, 10 bonding and 8 antibonding electrons resulting in a b o of 1 which agrees nicely with the known fact that F_2 has only a single bond. The pairing of all the electrons also explains the diamagnetic nature of fluorine

Ne_2· The 20 electrons here can be distributed into 5 bonding and 5 antibonding orbitals. The b.o., thus, becomes zero, showing thereby that Ne_2 cannot exist as a stable molecule.

This completes our treatment of the m.o. method We have applied the method to only homonuclear diatomic molecules because their treatment is relatively simple. However, the examples discussed do show most of the essential ideas of this approach. The m.o. theory can be applied to heteronuclear diatomic as well as to polyatomic molecules, but these topics are beyond the scope of this book. The m.o and valence bond methods are the two main approaches that a chemist uses to understand molecular behaviour in terms of electronic structure You may wonder why there are two and not only one approach to this problem The answer is that electronic description of molecular structures is a very complex problem and it still has not been completely solved. Chemists have, therefore, devised approximate ways of resolving the problem It turns out that one can do this in two different ways, and that is why there are these two approaches You may also wonder if one method is superior to the other. The answer is that each of them has some advantages and disadvantages and neither can be considered superior to the other. The valence bond method is attractive because it is close to a chemist's traditional view of a chemical bond. The m.o. method has the advantage that it is close to treatment of electronic structure of atoms. Linus Pauling, who was one of the pioneers in developing our understanding of chemical bond has summarized the situation in the statement · "The theory of chemical bond is still far from perfect. Most of the principles that have been developed are crude, and only rarely can they be used in making an accurate quantitative prediction However, they are the best that we have, as yet, and I agree with Poincare that 'it is far better to foresee even without certainty than not to foresee at all' "

Chemical bonding is one of the many areas in chemistry which will be hopefully tackled by future generations of chemists, like you.

2.3 HYBRIDIZATION—FURTHER EXAMPLES

We return now to the valence bond approach which was employed in Part I to discuss molecular structures. It was shown there that the idea of promotion-cum-hybridization has to be introduced to explain the nature of compounds formed by boron, beryllium and carbon In all these cases, promotion took place from 2*s* and 2*p* orbitals and hybridization involved the *s* and *p* orbitals. Properties of resulting hybrid orbitals are summarized in Table 2.1.

TABLE 2.1

Properties of Hybrid Orbitals

Name	*s*-Character	*p*-Character	Bond angle	Geometrical arrangement	Examples of molecules
sp diagonal	/2	1/2	180°	Linear	BeH_2, $HgCl_2$, C_2H_2
sp^2 trigonal	1/3	2/3	120°	Coplanar Triangular	BF_3, NO_3^-, C_2H_4, CO_3^{2-}
sp^3 tetrahedral	1/4	3/4	109°	Tetrahedral	BH_4^-, NH_4^+, CH_4, ClO_4^-, $SnCl_4$

Let us now consider compounds of some elements of the third period. The electronic configurations of phosphorus and sulphur show that the atoms of these elements have 5 and 6 electrons, respectively in the 3*s* and 3*p* orbitals taken together. In the ground state, these atoms have (like nitrogen and oxygen) three and two half-filled orbitals Thus, they form compounds like PF_3 and H_2S which are analogous to NF_3 and H_2O But phosphorus and sulphur also form compounds like PF_5 and SF_6 Since NF_5 and OF_6 are not known, it is obvious that some new feature must be present in the elements of the third period. This feature is the presence of vacant $3d$ orbitals which are comparable in energy to the occupied $3s$ and $3p$ orbitals. The paired electrons in the latter can, therefore, be unpaired by promotion to the vacant $3d$ orbitals leading to covalencies of 5 and 6. Hybridization can now involve not only the s and p orbitals but also the d orbitals yielding molecular geometries not found amongst compounds of the second period elements

In phosphorus, the ground state valence electron configuration is $3s^23p_x^13p_y^13p_z^1$ Excitation or promotion of one s electron to the $3d$ orbital gives the configuration $3s^13p_x^13p_y^13p_z^13d^1$ One of s, three of p, and one of d orbitals hybridize to form 5 sp^3d (hybrid) orbitals (Fig. 2.5), which point to the corners of a trigonal bipyramid The 5 orbitals are not equivalent but fall into two groups One group of three orbitals forming a plane is directed towards the corners of an equilateral triangle while the other group of two equivalent orbitals is perpendicular to the plane of the triangle, above and below it The experimentally determined structure of PCl_5 is in complete agreement with this picture. The molecule has trigonal bipyramidal geometry with the three equatorial chlorine atoms being closer to the central phosphorus atom than the two out-of-plane chlorine atoms

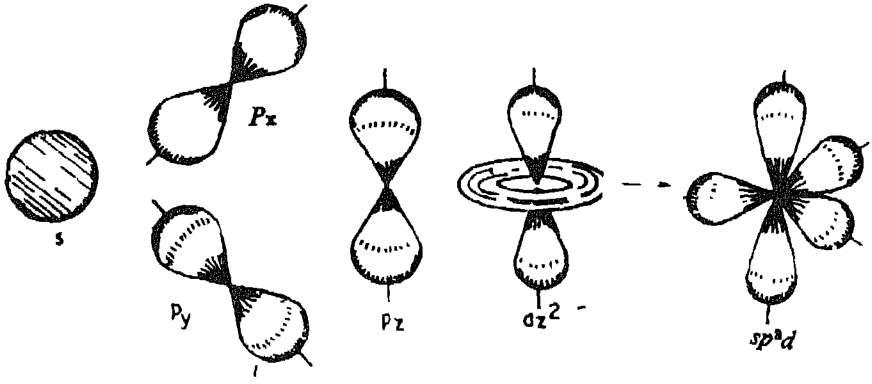


Fig. 2.5 The formation of five sp^3d hybrid orbitals These orbitals define a trigonal, bipyramid geometry.

The ground state valence electron configuration of sulphur is $3s^23p_x^23p_y^13p_z^1$. Promotion of two electrons, one each from $3s$ and $3p_x$ orbitals, to two of $3d$ orbitals followed by hybridization of one of *s*, three of *p*, and two of *d* orbitals leads to six sp^3d^2 hybrid orbitals. These are directed to the corners of a regular octahedron. The octahedral structure of SF_6 molecule is thus easily understandable (Fig. 2.6). Table 2.2 summarizes some of the hybridization schemes involving *d* orbitals which you will encounter in the study of transition metal chemistry

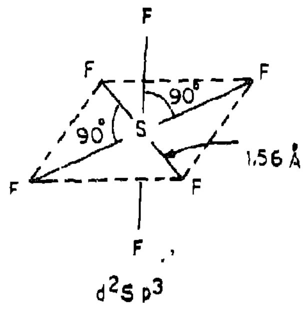


Fig. 2.6 Octahedral structure of SF_6.

2.4 BOND DISTANCE AND BOND ENERGY

An important characteristic of a chemical bond is its length. Bond lengths or bond distances can be obtained from experimental measurements as we shall study in the next section. Consider HCl, H_2 and Cl_2 molecules. The bond lengths, *r*, in these molecules have been found to be as follows:

$$r_{H-Cl} = 1.36\text{Å}$$

$$r_{H-H} = 0.74\text{Å}$$

$$r_{Cl-Cl} = 1.98\text{Å}$$

It can be seen that:

$$r_{H-Cl} = \tfrac{1}{2}r_{H-H} + \tfrac{1}{2}r_{Cl-Cl}$$

TABLE 2.2

Hybrid Orbitals and Molecular Shapes

Shape of molecule	Hybrid type	Atomic orbitals	Bond angle	Examples
Linear	sp	$s+p$	180°	$BeCl_2$, $HgCl_2$
Planar	sp^2	$s+2(p)$	120°	BF_3, BCl_3, CO_3^{2-}, NO_3^-
Tetrahedral	sp^3	$s+3(p)$	109°	CH_4, NH_4^+, BH_4^-
Square planar	dsp^2	$d+s+2(p)$	90°	$Ni(CN)_4^{2-}$, $[PtCl_4]^{2-}$
Trigonal bipyramidal	dsp^3	$s+3(p)+d$	90°,120°	PF_5 (g)
Octahedral	sp^3d^2	$2(d)+s+3(p)$	90	$[CrF_6]^{3-}$, SF_6 $[Co(NH_3)_6]^{3+}$

This equation will be easy to understand if we consider atoms as billiard balls, and assume that they are in contact in a molecule. The billiard ball model means that the radius of the hydrogen atom will be half of the bond distance in H_2 molecule.

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*The sequencing of orbitals in column 2 will depend on the nature of the central atom involved in the formation of molecule or ion.

Similarly, the radius of the chlorine atom will be half the bond length in Cl_2 molecule It follows that the HCl bond distance should be the sum of the radii of the two atoms in agreement with the above equation Fig 2 7 shows a pictorial view of this process

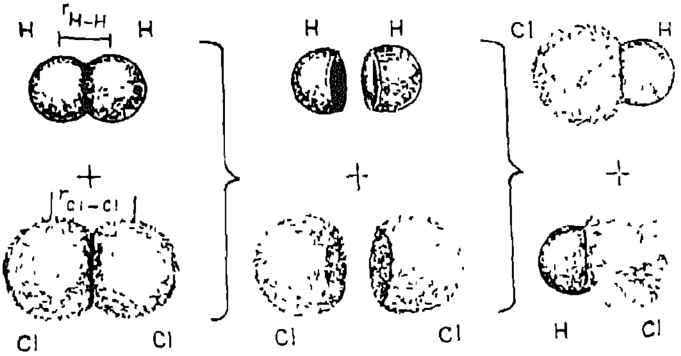


Fig 2.7 A pictorial view of the formation of two HCl molecules from a H_2 and a Cl_2 molecule

Our analysis shows that it is convenient to think sometimes that an atom is like a billiard ball One can then talk of the radius of the atom The length of the bond between two atoms whose radii are known, is just the sum of their radii However, the billiard ball model of an atom must be used with care We know from the earlier discussion about orbitals that atoms do not have sharp boundaries like balls The model, therefore, cannot be successful under every circumstance, and we should not expect bond lengths calculated from a fixed set of atomic radii to always agree with the experimental values For example, the C-C distance calculated from carbon atom radius (obtained from the C-C distance in diamond) should be 1.54Å This agrees perfectly with the C-C distance measured in ethane (C_2H_6), but disagrees with the C-C distances found in ethylene (1 33Å) and acetylene (1.20 Å) The fact that we are dealing here with different types of C-C bonds (i.e. single-bond in ethane, double bond in ethylene and triple bond in acetylene) having different types of hybridization (i.e. sp^3 sp^2, etc.) is primarily responsible for the disagreement It is found that if we adopt different sets of radii for atoms in different bonding situations, we are more successful in predicting bond lengths for a large number of bonds. Table 2.3 lists single and multiple

TABLE 2 3

Covalent Bond Radii

Single bond radii (Å)						Multiple bond radii (Å)
H	0 28	P	1 10	Te	1 37	C=0 67
C	0.77	As	1.21	F	0.64	C≡0.61
Si	1.17	Sb	1.41	Cl	0 99	N≡0.55
Ge	1.22	O	0.66	Br	1 14	
Sn	1.40	S	1.04	I	1.33	
N	0.70	Se	1.17			

bond radii of some atoms. Atomic radii for double bonds are about 14% and those for triple bonds about 23% smaller than the radii obtained for single bonds A similar set of radii can be obtained for ions from ionic solids.

Bond energy : The energy required to break a bond is called the bond energy. For a gas like hydrogen with a diatomic molecule, H_2, the *dissociation energy* of the substance is identical to the bond energy of the molecules. For a polyatomic molecule like H_2O having two bonds, the bond energy of the O-H bond is taken as half of the energy required to dissociate H_2O molecules in vapour into oxygen and hydrogen atoms The N-H bond energy is, similarly, one-third of the energy required to dissociate NH_3 molecules into atoms.

The reasoning used for interpreting bond lengths can also be used for bond energies. Consider the HI molecule formed from H_2 and I_2 molecules. One may say that the share of each hydrogen atom in the bond energy of HI molecule is half of the value of the bond energy in H_2 molecule. Similarly, the share of each iodine atom in the bond energy of HI molecule is also half of the bond energy of I_2 molecule. The energy of the H-I bond should then be just the sum of the contributions of hydrogen and iodine atoms. Let us see how tenable this idea is.

The experimental bond energies of H_2 (ε_{H-H}) and I_2 (ε_{H-I}) are 435.4 kJ mol^{-1} and 150.6 kJ mol^{-1}. The calculated bond energy of HI (ε_{H-I}) then should be :

$$\varepsilon_{H-I} = \tfrac{1}{2}\,\varepsilon_{H-H} + \tfrac{1}{2}\,\varepsilon_{I-I} = 217.7 + 75.3 = 293.0 \text{ kJ mol}^{-1}$$

This is in good agreement with the measured value of 297.1 kJ mol^{-1}.

The above method of calculating bond energies works only for molecules involving similar types of bonds. The single bond energies of some common bonds are given in Table 2.4.

TABLE 2.4

Energies of Some Typical Bonds

Bond	Bond energy (kJ/mol)	Bond	Bond energy (kJ/mol)	Bond	Bond energy (kJ/mol)	Bond	Bond energy (kJ/mol)
F-F	159.0	O-F	184.1	C-F	485.3	H-O	464.4
Cl-Cl	242.7	C-O	355.6	N-Cl	200.8	N-H	389.1
Br-Br	192.5	H-F	564.8	C-Br	276.1	C-Cl	326.4
I-I	150.6	H-Cl	430.9	I-Cl	209.2	Si-I	213.4
H-H	435.1	H-I	297.1	C-H	414.2	P-Br	272.0
C-C	347.3			S-Cl	251.0		

2.5 METHODS OF DETERMINING MOLECULAR STRUCTURE

It was mentioned in Part I that the most widely used methods for determining structure fall into two main categories which are · (i) spectroscopic methods, and (ii) diffraction methods. We shall now consider he subject of molecular spectroscopy in some detail.

All spectroscopic methods involve study of either absorption of radiation (absorption spectroscopy) or of emission of radiation (emission spectroscopy). The former is generally more convenient and is, therefore, more popular. In an absorption spectroscopy experiment, a sample is exposed to a beam of radiation The frequency of radiation is changed continuously, and the intensity of radiation which has passed through the sample (transmitted radiation) is measured It is observed that for definite values of frequencies, the intensity of transmitted radiation falls, showing thereby that the radiations corresponding to these frequencies are absorbed by the sample. The plot of intensity versus frequency is known as the absorption spectrum of the sample A typical spectrum is shown in Fig. 2.8.

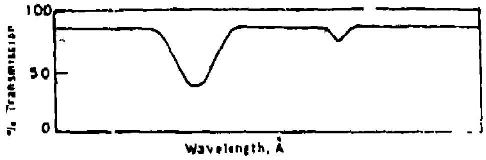


Fig. 2.8 A typical absorption spectrum—the minima correspond to the wavelength absorbed by the sample.

The reason why only certain frequencies, and not all frequencies, are absorbed by the sample is easy to understand We know that molecules, like atoms, have quantized energy levels, which means that they can have only certain but not all values of excitation energies. If a molecule is at a particular energy level and if there exists another energy level above it, the molecule can make the transition to the upper level by absorbing an appropriate radiation. If the difference in energies of the two levels is $\triangle E$, then only such radiation will be absorbed whose frequency, ν, is related to the energy gap $\triangle E$ by the equation, $\triangle E = h\nu$. Since the quantized energy levels are characteristic of a molecule, the set of frequencies absorbed (i.e. the absorption spectrum) is also characteristic of a molecular species. The absorption spectrum of a substance can, thus, be used to identify its molecule. Further, since the energy levels depend on such structural parameters of molecules as bond lengths, bond angles, etc., it is clear that molecular spectra can enable one to determine the structures of molecules.

Molecular spectra are of several types because, unlike atomic energy levels, molecular energy levels are of various types. First, we have electronic energy levels which are associated with the motion of electrons in a molecule. These are the energy levels of the various m.o. in a molecule The separation of electronic levels is of the order of 420 kJ mol^{-1}. Transitions between these levels are, therefore, brought about by radiations in the ultraviolet and visible regions. The branch of molecular spectroscopy, in which transitions between electronic energy levels are studied, is known as *electronic spectroscopy or ultraviolet-visible spectroscopy*.

Apart from electronic levels, molecules have energy levels due to the following

(i) *Vibrations* : These are associated with the stretching and bending of chemical bonds due to small shifts in the positions of atoms in molecules.

(ii) *Rotations* · These are due to rotations of molecules in space.

Vibrational and rotational energy levels are also quantized. The energy spacings ($\triangle E$) between vibrational levels correspond to radiations in the infrared region, while the spacings of rotational levels correspond to radiations in the microwave region. Vibrational and rotational spectroscopy are, therefore, also known as *infrared spectroscopy* and *microwave spectroscopy*, respectively

The rotational energy levels of a diatomic molecule are related to its moment of inertia which in turn is related to the masses of involved atoms and the bond length Microwave absorption frequencies yield information about energy gaps, $\triangle E$, from which moments of inertia and hence, bond lengths can be calculated. A polyatomic molecule may have three different moments of inertia and the expressions for its rotational energy levels are quite complex Nevertheless, bond distances and bond angles can be derived from absorption spectra of polyatomic molecules

The spacings of vibrational energy levels are primarily determined by the *stiffness* of chemical bonds Infrared spectra yield information about stiffness of bonds in terms of force constants. Some molecular groupings like $C=O$, $C\equiv C$, $-NO_2$, $C-H$, etc. have characteristic vibrational absorption frequencies. The presence of such groups in a molecule of unknown structure can be easily established from the vibrational spectrum of the substance The infrared spectrum is, thus, an extremely valuable tool for the determination of molecular structures

The electronic absorption spectrum can similarly be correlated with specific functional groups. Thus, each of the $C-C$, $C=C$, $C\equiv C$, $C=O$, $C-H$, etc. groupings absorb in specific frequency regions. The ultraviolet and visible spectra are, therefore, also useful for identification of functional groups

Apart from electronic, vibrational and rotational energy levels, molecules also have energy levels due to nuclei (*Mossbauer spectroscopy*), due to interaction of nuclear spins with external magnetic field [*nuclear magnetic resonance* (*NMR*) *spectroscopy*], and due to interaction of electron spin with external magnetic field [*electron spin resonance* (*ESR*) *spectroscopy*]. All these methods are used in modern chemistry to unravel the structures of molecules and you will study them in advanced courses

EXERCISES

2.1 (a) What do you understand by a molecular orbital (m.o.) ? What is the maximum number of electrons that can occupy a molecular orbital ?

(b) How many m o 's of H_2 originate from the hydrogen 1*s* atomic orbitals ?

2.2 What do you mean by bonding and antibonding molecular orbitals ? Give the number of electrons which occupy the bonding in H_2+, H_2 and He_2

2.3 Use the energy level diagram to show that N_2 would be expected to have a triple bond, F_2 a single bond and Ne_2 no bond.

2.4 What is meant by bond order ? Calculate the bond order of He_2+, O_5- and O_2- molecules

2.5 Explain the paramagnetic behaviour of oxygen with the help of energy level diagram

2.6 Explain in terms of valence bond theory the following observations ·

(i) CCl_4 and $SiCl_4$ are both tetrahedral
(ii) CO_2 is linear but SO_2 is angular
(iii) BF_3 is planar but NH_3 is not
(iv) HSH angle in H_2S in closer to 90° than HOH angle in H_2O

2 7 Predict on the basis of electron pair repulsion theory the geometry of the following molecules SF_6, $HgCl_2$, NH_4^+, $Ni(CN)_4^{2-}$

2 8 (a) What do you mean by the term bond energy ? How would you calculate the bond energy of a molecule ?

(b) The bond energies of H_2 and I_2 are 435 4 kJ mol^{-1} and 150 6 kJ mol^{-1} respectively Calculate the bond energy for HI molecule.

2 9 Why are the bond angles in CH_4, NH_3 and OH_2 different, when tetrahedral structure is held valid for all of them ?

2 10 What is meant by spectrum and how is it obtained ?

2.11 Write short notes on .

(i) Valence bond model
(ii) Hybridization
(iii) Bond distance
(iv) Determination of molecular structure.

UNIT 3

More About States of Matter

The reasons for substances being found in different states as gases, liquids and solids have been dealt with in Unit 5 of Part I. The general characteristics of solids are described in section 5.7 of that Unit. Differences in the nature of bonding or attractions between constituent particles lead to formation of different types of solids (Sec. 4.9 of Part I). Substances which are solids at ordinary temperatures will consist of highly polar molecules, oppositely charged ions in equivalent numbers or cations and electrons to make up electrically neutral substances. In this Unit, we shall discuss more about crystalline state of solids and about water which is a liquid with very unusual properties.

3.1 CLASSIFICATION OF SOLIDS

Different structural features of solids can form the basis for classifying them They may be roughly divided into two classes· *true solids* and *pseudo solids* A distinctive feature of solids is that they are rigid A true solid has a shape which it holds against mild distorting forces A pseudo solid lacks this character It can be more easily distorted by bending and compressing forces. It may tend to flow slowly even under its own weight and lose shape Pitch and glass are two examples of pseudo solids. In old buildings, window glasses are found to have become somewhat thicker at the bottom and thinner near the top. The rigidity and shape of pseudo solids are only apparent. Such substances are better described as *supercooled liquids* We shall not pursue their study at present except to say one thing· pseudo solids do not melt sharply on being heated, they gradually soften over a wide range of temperatures and eventually lapse into a liquid state.

Solids may exist in shapeless *amorphous* forms or in well shaped *crystalline* forms. Crystalline solids may be further classified according to the nature of particles constituting them and the binding forces between them (Table 3 1).

Amorphous solids include substances like glass, fused silica, rubber and polymers of high molecular masses They may even have small parts in crystalline and rest in non-crystalline form. Crystalline parts of an otherwise amorphous substance are called *crystallites.* When we try to cut a crystalline solid with a sharp edged tool it

TABLE 3 1

Crystal Types According to Constituent Particles

Crystal type	Constituent particles	Major binding forces	Properties	Examples
Molecular	Small molecules	van der Waals forces	Soft, low melting volatile, electrical insulators, poor thermal conductors, low heats of fusion	Solid CO_2, and CH_4, Wax, iodine, ice, sulphur
Ionic	Network of positive and negative ions systematically arranged	Strong electrostatic attractions	Brittle, high m.p., poor conductors of electricity and heat, very high heats of fusion	Salts like NaCl, LiF, $BaSO_4$
Covalent	A network of chemically bound atoms of one or more kinds	Covalent bond forces	Very hard, high m p., poor conductors of heat and electricity, high heats of fusion	Diamond, silicon, quartz
Metallic	Positive ions in a sea of electrons	Electrical attraction	Very soft to very hard low to high m p., good conductors of electricity and heat, metallic lustre, ductile and malleable, moderate heats of fusion	Common metals and some alloys

gives a clean cleavage, but an amorphous substance gives an irregular or conchoidal fracture (Fig. 3.1) Crystalline substances have a definite rigid shapes or morphology. Every crystal is contained within a well defined set of surfaces which are called *planes*. Such a substance also has : (i) a sharp melting point, (ii) a characteristic heat of fusion, (iii) a definite three dimensional arrangement of constituent particles. and (iv) general incompressibility.

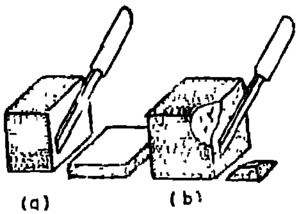


Fig 3 1 The cutting of solids : (a) A crystalline solid gives a clean cut, (b) An amorphous solid gives an irregular cut.

3.2 X-RAY STUDIES OF CRYSTALS

Much of our information about the structures of crystals at the level of molecules, atoms and ions has been revealed by their interactions with X-rays. Crystals are found to act as diffraction gratings for X-rays. This indicates that the constituent particles in crystals are arranged in planes at close distances in repeating patterns. W. L. Bragg and his father W. H. Bragg tried to locate relative positions of Zn and S atoms in a ZnS crystal by a detailed analysis of diffraction patterns formed with X-rays. Later, a method was developed by Debye, Scherrer and Hull in which the X-ray pattern could be obtained for a substance in powdered form instead of a single crystal. The diffraction pattern was taken on a circular film surrounding the powder target. Fig. 3 2 shows one of such diffraction pictures.

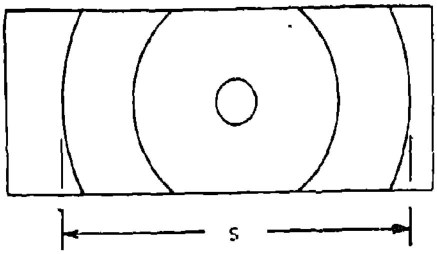


Fig 3 2 Diffraction pattern yielded by Debye-Scherrer-Hull powder technique.

To decide about distances between constituent particles in a crystal from the pattern shown in Fig 3 2 is a problem in physics, and we shall not go into its details in the present course We shall refer here only to the involved basic law known as Bragg's law. This is given by the following equation ·

$$n\lambda = 2d \sin \theta \qquad (3\ 1)$$

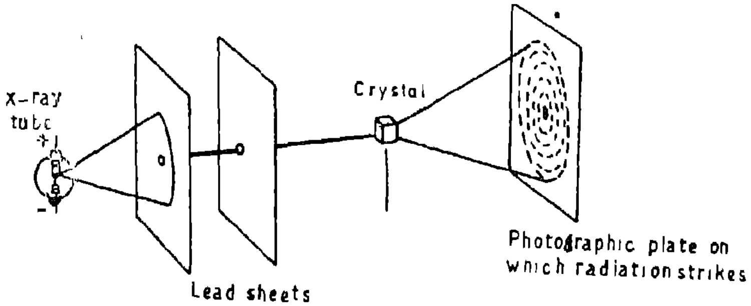


Fig 3.3 (a) A simple set-up for X-ray diffraction

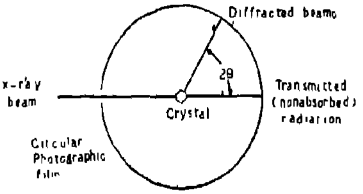

Diffracted beams
2θ
x-ray beam
Crystal
Transmitted (nonabsorbed) radiation
Circular Photographic film

Fig. 3.3 (b) Simplified representation of X-ray diffraction (in real situation many spots appear).

Here d is the distance between planes of the constituent particles in the crystal, parallel to the plane on which the X-rays are incident, 2θ is the angle made by a diffracted X-ray beam with the direction of the incident beam, λ is the wavelength of X-rays used, and n is an integer (1, 2, 3, etc) which stands for the serial order of diffracted beams Using Bragg's law we can calculate distances between repeating planes of particles in crystals or using crystals with known interplanar distances we can calculate the wavelengths of the X-rays used.

Example 3 1

What will be the wavelength of the X-rays which give a diffraction angle, 20 equal to 16.80° for a crystal, if the interplanar distance in the crystal is 0.200 nm and only first order diffraction is observed?

Solution

In the equation, $n\lambda = 2d \sin \theta$, n is equal to 1. Therefore,

$\lambda = 2 \times 0.2 \times 10^{-9}\text{m} \times \sin 8.40 = 0.4 \times 0.146 \times 10^{-9}\text{m} = 0.0584 \times 10^{-9}\text{m}$ or 0,584 Å

3.3 CRYSTAL LATTICES AND UNIT CELLS

The three dimensional distribution of constituent particles in a crystal can be found on the basis of diffraction of X-rays from the different faces of a crystal. Fig. 3.4 is an example of a three dimensional diagrammatic representation of a crystal However, in the crystal, the constituent particles are packed as closely as possible. A representation of a crystal like Fig. 3.4, in which the locations of constituent particles are shown by points, is called the *space lattice* or *crystal lattice* of the crystal. For every crystal lattice it is possible to select a group of lattice points which sets the pattern for the whole lattice. This three dimensional group of points is called the *unit cell* of the crystal and it is characterized by the distances a, b and c along the three edges of the unit cell and the angles α, β and γ between the pairs of edges (b, c), (c, a) and (a, b) respectively (Fig 3.4). The whole crystal can be developed by a step-wise shifting of the unit cell in all the three directions. It is like building a whole block with the help of bricks.

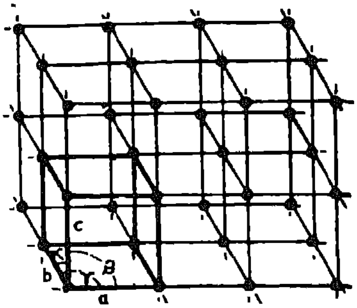
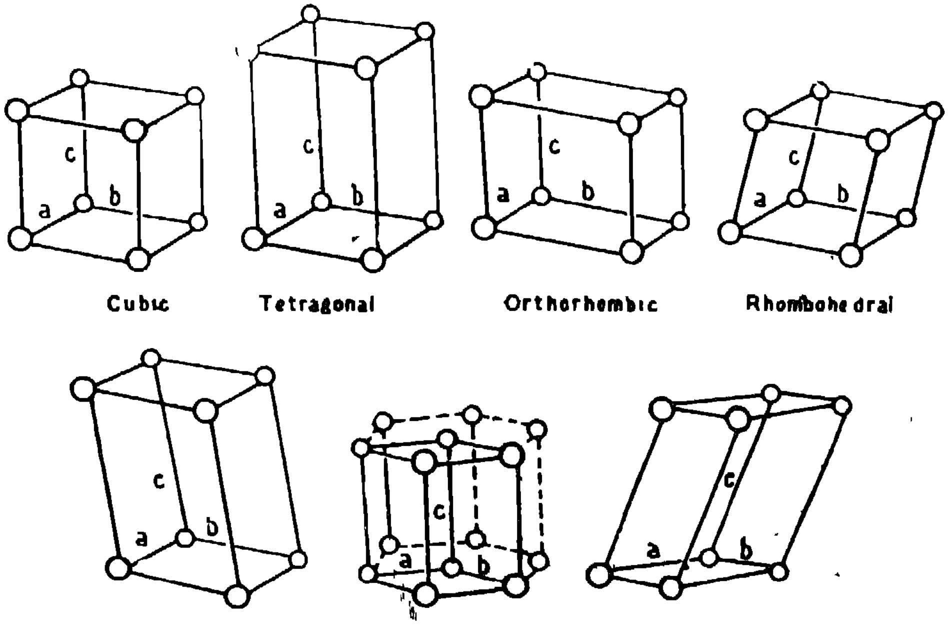


Fig. 3.4 A simple depiction of crystal lattice and unit cell (the whole crystal is like a brickwork, heavy lines show unit cell)

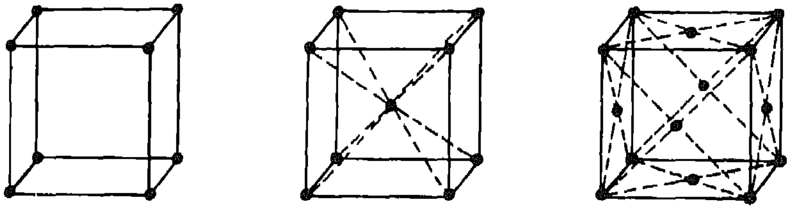


Cubic Tetragonal Orthorhombic Rhombohedral

Monoclinic Hexagonal Triclinic

Fig. 3.5 The seven primitive unit cells in the crystals

In all seven types (Fig 3 4) of *basic or primitive unit cells* have been recognized amongst crystals They are called *seven crystal systems* or *crystal habits* These are shown in Fig 3.5 and their characteristics are listed in Table 3 2 In fact, a crystal consists of a large number of unit cells; this number depends on the size of the crystal. If the unit cell in a crystal lattice has lattice points only at the corners, the crystal is said to have a *simple lattice* There are seven simple lattices based on the seven primitive unit cells But all crystals do not have simple lattices Some are more complex and it is not possible to discuss all of these at this stage. However, if we consider the cubic system of crystals, besides the simple cubic crystals, we often meet two other types of *cubic crystals* (or *cubic lattices*). These are called *face centred cubic* (fcc) and *body centred cubic* (bcc) crystals. Unit cells of all the three cubic types of crystals are shown in Fig. 3.6.



Simple cubic

Body central cubic
(bcc)

Face centred cubic
(fcc)

Fig. 3 6 Three types of unit cells for cubic crystals

During crystallization all faces of a crystal do not grow at the same rate and, therefore, all crystals of a substance may not have the same ratio of axial edges as for the unit cell, but they will have the same axial angles Actual crystals can differ in their final shapes and yet they may have unit cells of the same type.

TABLE 3 2

Different Crystal Systems

System	Axial distances	Axial angles	Examples
Cubic	$a=b=c$	$\alpha=\beta=\gamma=90^\circ$	Copper, Zinc blende, KCl
Tetragonal	$a=b\neq c$	$\alpha=\beta=\gamma=90^\circ$	White tin, SnO_2
Orthorhombic	$a\neq b\neq c$	$\alpha=\beta=\gamma=90^\circ$	Rhombic sulphur
Monoclinic	$a\neq b\neq c$	$\alpha=\gamma=90^\circ,\ \beta\neq 90^\circ$	Monoclinic sulphur
Hexagonal	$a=b\neq c$	$\alpha=\beta=90^\circ,\ \gamma=120^\circ$	Graphite
Rhombohedral	$a=b=c$	$\alpha=\beta=\gamma\neq 90^\circ$	Calcite
Triclinic	$a\neq b\neq c$	$\alpha\neq\beta\neq\gamma\neq 90^\circ$	Potassium dichromate

3.4 PACKING OF CONSTITUENT PARTICLES IN CRYSTALS

In the formation of crystals, the constituent particles get closely packed together. The available space is used most economically and a state of maximum possible density is reached Since the constituent particles can be of various shapes, the mode of closest packing of particles will vary according to their shapes. We shall discuss here the packing modes of simple spherical particles to which the common constituent particles of crystals approximate We shall further limit ourselves to spheres of equal size. By placing such spheres in a row in horizontal alignment, we develop an edge of a crystal [Fig 3.7 (a)] By combining the rows we can build a crystal plane [Fig 3 7 (b)]

Combining of rows can be done in two ways with respect to the first row

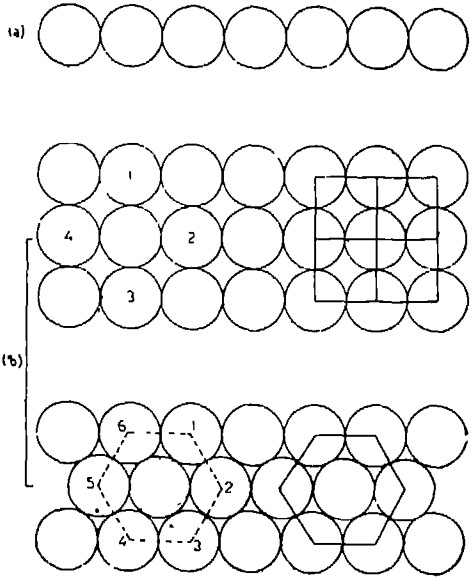


Fig 3 7 Packing of spheres for efficient use of available space . (a) Edge formation, (b) Two modes of plane formation

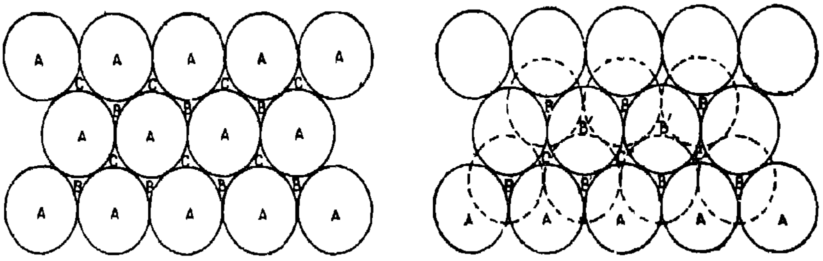
(i) The particles in the adjacent rows may show a horizontal as well as a verticle alignment and form squares. This type of packing is called a *square close packing*.

(ii) The particles in every second row are seated in the depressions between particles of the first row The particles in the third row will be vertically aligned with those in the first row, and so on. This arrangement gives hexagonal patterns and is called a *hexagonal close packing*

The second mode of packing is evidently a more efficient one. It leaves less space unoccupied by spheres. In square close packing, a central sphere is in contact with four other spheres and in the hexagonal close packing, a central sphere is in contact with six other spheres [Fig 3 7 (b)].

For two dimensional packing, a hexagonally close packed layer gives a more efficient packing. Based on this, let us proceed further to consider a three dimensional packing maintaining a hexagonal close packed pattern for the layers. Fig 3 8 (a) shows the base layer in a crystal

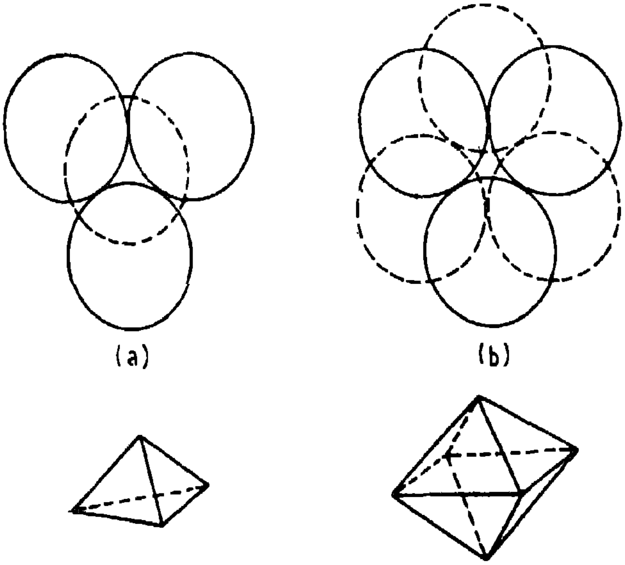
In this layer, let the spheres be marked with the letter A and two types of voides left between the spheres be marked with the letters B and C as shown in Fig 3.8 (a) If a second layer is placed with spheres vertically aligned with those in the first layer, its voids will also cover the voids in the first layer. This will amount to an inefficient filling



(a) (b)

Fig 3 8 Layers in close packing of spheres · (a) The hexagonal close packed base layer, (b) Two layers together

of space. If we arrange the second layer so that its spheres are seated in the *B* voids of first layer, the *C* voids will remain unoccupied as no sphere can be seated in them under this plan [Fig 3 8 (b)] In the second layer thus placed, we shall have some second layer voids over the *C* voids of the first layer. We shall call these voids (made of two voids in two different layers) as *C'* voids There will also be ordinary voids in the second layer over the positions of spheres in the first layer We can call these as *B'* voids of second layer. While the *B* and *C* voids of first layer are both triangular in shape, in the second layer, only the *B'* voids are triangular The *C'* voids of second layer are combinations of two triangular voids of first and second layers with one triangle vertex upwards and the other triangle vertex downwards. A simple triangular void in a crystal gets surrounded by 4 spheres and is called a *tetrahedral* void or hole. A double triangular void like *C'* gets surrounded by 6 spheres and is called an *octahedral* void (Fig 3.9).



(a) (b)

Fig. 3.9 Two types of voids in crystals . (a).Tetrahedral void, (b) Octahedral void

If a third layer is placed over the second layer, so that the spheres cover the tetrahedral or B′ voids, we get one type of three dimensional closest packing in which the spheres in every third or alternate layers are vertically aligned. This pattern is called the AB AB. . pattern. Alternatively, if the third layer sphere cover the octahedral or *C′* voids, we get a packing in which spheres in every fourth layer will be vertically aligned. This gives the ABC ABC .type pattern of stacking spheres Both stacking methods are equally efficient though different in form. They can be repeated to any length. In a three dimensional packing of spheres the AB AB. . .packing is called the *hexagonal close packing* (hcp) and the ABC ABC .packing is called the *cubic close packing* (ccp). The ccp type packing tallies with the fcc type packing described earlier Molybdenum, magnesium and beryllium crystallize in the hcp structure Iron, nickel, copper, silver, gold and aluminium crystallize in the ccp structure

The voids or holes in crystals are also called *interstices* Their sizes acquire importance when some non-lattice atoms (such as H, B, C, N) or ions are to be accommodated in them. Transition metals when they form crystals of hydrides, borides, carbides, and nitrides, respective non-metals are accommodated in the interstices.

Coordination Number . In the hcp and ccp modes of stacking, a sphere will be in direct contact with 6 other spheres in its own layer. It will also be directly touching 3 spheres in the layer above and 3 in the layer below Thus, a sphere has 12 closest neighbours in hcp and ccp stacks It is said to have a *coordination number* of 12. In any crystal lattice, the number of closest neighbours of any constituent particle is called its coordination number. Coordination numbers of 4, 6, 8 and 12 are quite common in various types of crystals.

3 5 IONIC CRYSTALS

This group of crystals are made from cations and anions, in alternate positions, so that an overall electrical neutrality exists in the crystal. The two types of charges are present in equivalent amounts. The cations and anions will generally be of different sizes. The voids in such crystals will be wider than those in packings of equal spheres (in metals). In an ionic crystal, we have two interpenetrating lattices of anions and cations. Sodium chloride crystal is a typical example. In NaCl, it has been determined that distance between two adjacent ions is 2.81Å. If we add the radii of sodium (0.95Å) and chlorine (1.81Å), it shows that there is a little space between the ions. Structure of solid NaCl is a special class of ionic crystals. Chlorides, bromides and iodides of lithium, sodium, potassium and rubidium (as well as some halides of silver) ordinarily possess the NaCl structure in which coordination number of each ion is 6. It is to be remembered that every ion in the crystal interacts with every other ion, so that the whole crystal can be considered as a single *giant molecule.*

Unlike metallic crystals, ionic crystals have different types of constituent particles in neighbouring positions. This difference obstructs any easy slip between neighbouring units in an ionic crystal. Thus, ionic crystals are liable to break under stress while metals show the properties of ductility and malleability.

In an ionic crystal lattice, constituent ions are held together by strong electrostatic forces. Therefore, ionic solid compounds have fairly high melting points, e.g Na_2SO_4 an ionic solid has the m p. of 1157 K.

3 6 DEFECTS IN CRYSTALS

Perfectly crystalline substances are very scarce in nature When we do get crystalline minerals in a reasonably defect-free form, we regard them as jewels and are prepared to pay heavy prices for them The imperfections may occur even in chemically pure crystalline substances due to irregularities during growth of crystals These are called *physical, intrinsic* or *native defects* Impure crystalline substances may have physical defects, but in addition they have *chemical* or *extrinsic defects* also. The term *defect* generally denotes departure from regularity in the arrangement of the constituent particles (atoms, ions and molecules) in a crystal. Defects in crystals greatly influence their physical properties (e.g electrical conductivity and diffusion) and sometimes even their chemical properties. Here, we shall refer briefly to only a few of these aspects

Point Defects We have learnt about a crystal lattice being a regular repeating arrangement of points representing relative locations of its constituent particles. If any of these particles is either missing from the crystal lattice or is dislocated to a position meant for another particle or shifts to an interstitial position, we get a *point defect.* Here, we shall consider point defects of ionic crystals In such defects, electrical neutrality of the crystal is maintained and stoichiometry is not affected.

When a cation and an anion are missing from their normal positions in the crystal lattice, we get voids or vacancies in the crystal Existence of such paired vacancies at lattice points is called a *Schottky defect* [Fig 3 10 (b)] after the German scientist, Schottky, who discovered it in 1930 If, however, an ion is not completely missing but shifts to an interstitial position in the lattice leaving a vacancy in its own position, it constitutes a *Frenkel defect* [Fig 3.10 (c)] discovered by the Russian scientist Frenkel in 1926. Though vacancies are generated both in Schottky and Frenkel defects, the former leads to a decrease in the overall density of the crystalline substance but the latter does not.

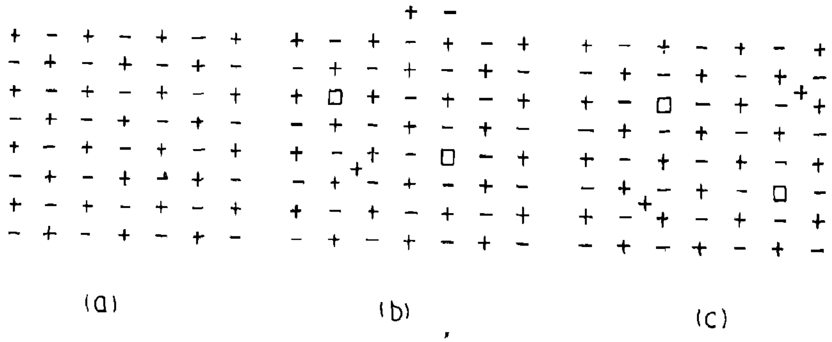


Fig 3 10 (a) Ideal crystal, (b) Crystal with Schottky defects, (c) Crystal with Frenkel defects.

Another interesting defect observed in ionic crystals is due to neutral atoms occupying some of the interstitial positions These do not disturb electrical neutrality Thus, Zn atoms can be trapped in ZnO crystals [Fig 3 11 (a)] Yet another defect arises from substituting ions of one valency state by those of another valency state Thus, two out of three ferrous ions in a lattice may be converted to ferric state and the third ferrous ion may be removed from a lattice site. This happens in iron pyrites. Existence of ferrous and ferric ions side by side provides an opportunity for free electron exchange Such a facility gives rise to metallic lustre and, coupled with the natural colour of iron pyrites, some samples of the mineral shine like gold and have been nick named *fools' gold* The defects of this kind where electron flow is facilitated because of different oxidation states of atoms existing side by side can also generate metallic conduction in non-metallic substances. The existence of several such defects sites together in a crystalline substance may be exhibited in the substance having a non-stoichiometric formula Non-stoichiometric formulae are common in sulphides and oxides Cuprous sulphide samples are found to analyse anything between $Cu_{1.96}S$ and Cu_2S. Non-stoichiometry in crystals is regarded as a *chemical or non-stoichiometric defect* These non-stoichiometric compounds show properties of semiconductors. Non-stoichiometric compounds were at one time called *berthollides* after Claude Berthollet who postulated that composition of a chemical compound could change with its method of preparation

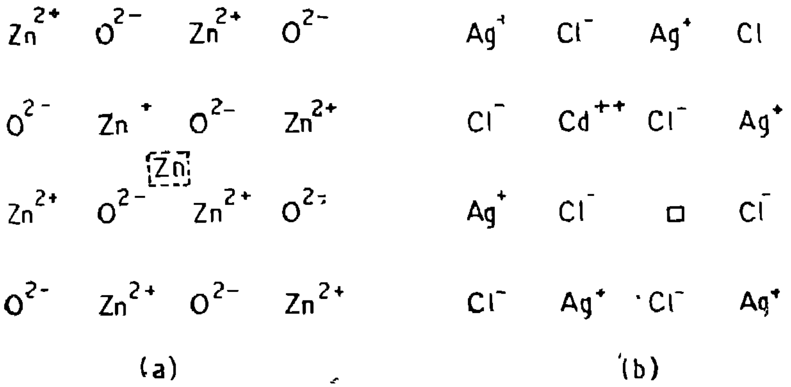


Fig. 3 11 Chemical or non-stoichiometric defects. (a) Zinc metal in the interstitial position of ZnO crystal, (b) Cation vacancy in AgCl by substitution of Cd^{2+} for Ag^+

In some crystal, the specific cation or anion may get replaced by an impurity ion of nearly equal size. If a Cd^{2+} ion takes the place of an Ag^+ ion in AgCl lattice in order to maintain electrical neutrality, another Ag^+ will be missing from the lattice point to create a vacancy [Fig 3 11 (b)] Such a vacancy can be helpful in electrical conductance through AgCl by migration of Ag^+ ions from lattice sites into vacant sites and so on. So, while Ag^+ ions move in one direction, the vacancies move in the other.

3.7 ELECTRICAL CONDUCTIVITY IN SOLIDS

We are familiar with high electrical conductivity of substances like copper or silver. When a bulb is connected with a battery through a copper wire it glows. We also are aware of the conductivity of graphite rod used as an electrode. It also can be seen that NaCl crystal, when put in a circuit, apparently does not conduct electricity. Based on the electrical conductivity, solids can be broadly classified into three types : metals, insulators and semiconductors Conductivity of solids varies anywhere from 10^8 ohm^{-1} cm^{-1} in metals to 10^{-22} $ohm^{-1}cm^{-1}$ in insulators. Conductivity of a solid substance is its characteristic property and reflects the internal structure and bonding in the solid.

Conductivity in metals is due to movement of free electrons in metal crystals. Most of the inorganic and organic solid compounds come under the category of insulators. Here, it would be relevant to mention that basically conductivity in any solid is due to movement of electrons, ions, charged interstitials or vacancies. Ionic solids conduct electricity to a very small extent though they come in the category of insulators. Conduction in ionic solids involves migration of ions or other charged species under an applied field. The ion migration becomes possible because of the presence of vacancies or interstitials in the ionic solids (which you have studied in the previous section). If an ion moves from its lattice site to occupy a 'vacancy', it creates a new vacancy and in this way a vacancy may migrate across a crystal, which is effectively the same as moving a charge in the opposite direction.

Semiconductors have conductivities between metals and insulators and these fall in the range 10^2 to 10^{-9} ohm^{-1} cm^{-1}. Germanium and silicon are the most common examples. The atoms of both have four electrons in the outer shell, which form four covalent bonds with other atoms and give rise to a tetrahedral structure like diamond. If sufficient energy is given, some of the covalent bonds break, and electrons are ejected from their normal sites. These electron can then migrate, leaving behind a positive charge where a bond is missing. Electrical conductivity takes place by migration of electrons one way, and migration of positive holes in the other. This is termed *intrinsic conductivity*. If some impurity is added, e.g. arsenic, the conductivity is enhanced Here, out of 5 valence shell electrons in arsenic, 4 form bond and the fifth can convey current quite readily. This is an example of *extrinsic conductivity*. You will study more details about semiconductors in your physics course.

Conductivity of metals generally decreases with increase in temperature while that of semiconductors increase with temperature.

3.8 ALLOYS

Alloys are metallic substances containing two or more elements, at least one of which is a metal. They often show crystal defects. These defects are largely responsible for the special properties of alloys. Small atoms of non-metals like hydrogen, boron, nitrogen and carbon are often taken up in the interstitial spaces or voids in metallic crystals. This is how carbon present in various steels and cast iron forms iron carbide.

There are two general types of alloys : (i) intermetallic compounds and interstitial compounds of metals with non-metals, and (ii) solid solutions of metals and non-metals in metals.

The solid solutions often involve substitutional and interstitial impurities Colloidal dispersion in metals are also sometimes treated as alloys Alloys, in which mercury is one of the metals, are called *amalgams.*

Some advantages of making alloys and their examples are given below ·

Advantage	*Example*
(i) To increase hardness	Alloying of iron with carbon and several other elements
(ii) To reduce corrosion	Making stainless steel from iron
(iii) To increase tenacity	Brass, an alloy of copper, is more tenacious than copper
(iv) To improve colour	Aluminium bronze (Al with 5% Cu) looks like gold
(v) To get better castings	Antimony is added to lead to make type metal
(vi) To lower melting points	Solder is an alloy of lead and tin
(vii) To modify chemical activity	Amalgams are usually made for this purpose

3.9 LIQUID CRYSTALS

Some crystalline substances on melting give non-uniform or anisotropic liquids (they do not have the same values of properties in all directions). The liquids formed show double refraction which is a property ordinarily associated with some solids but not with common liquids. In the state of *liquid crystals*, a substance has some properties of crystalline solids and the flow properties of liquids The temperature at which a substance changes sharply into the state of liquid crystals is known as its *transition point* A higher temperature at which it forms a clear, uniform or *isotropic* (same in all directions) liquid is given the usual name of melting point.

The state of liquid crystals is also called *mesomorphic* or *paracrystalline* state. Given below are examples of two substances forming liquid crystals.

	Transition point (*K*)	*Melting point* (*K*)
Para-azoxyanisole	389	408
Normal-octyl-para-azoxycinnamate	367	448

Liquid crystals are becoming important substances because of their electrical and optical properties and use in electronic display instruments

3.10 SOME UNUSUAL PROPERTIES OF WATER

A major part of all living organisms is made up of water Human body has about 65%, and some plants have as much as 95% water It plays a very important role in our daily life. not only because it is essential for us but also because of its very unusual properties. Water has a high specific heat which makes it a good storehouse of thermal energy. It has a greater density as liquid than as solid ice. This keeps ice floating on water and prevents floating of lower layers in lakes. It has high heats of vaporization and fusion So, water does not evaporate or freeze as easily as many other liquids would. A reasonably long temperature range between its freezing point and boiling point makes water a very convenient medium for chemical reactions and biological processes. The great dissolving power of water arises from its polar character and high dielectric constant.

The unusual magnitudes of various physical properties of water and its exceptional behaviour are linked with the structure of liquid water and polar character of its molecules. Because of hydrogen bonding, water molecules are held together, extensively forming networks of molecules. Liquid water retains in part the crystalline order of its solid form X-ray diffraction studies of liquid water support this hypothesis.

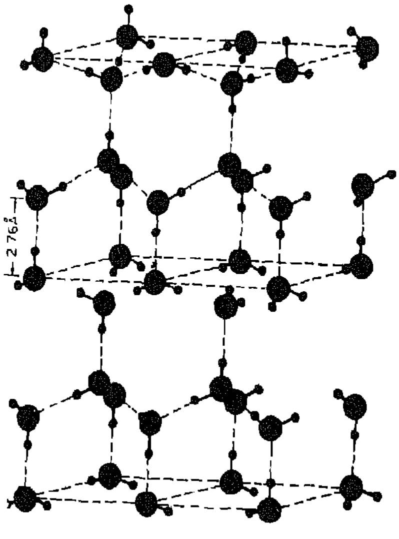


Fig 3.12 Structure of ice.

Examination of ice crystals with X-rays shows that each oxygen atom is surrounded tetrahedrally by four other oxygen atoms at a distance of 0.276nm (Fig. 3.12). Hydrogen bonding gives ice a rather open type structure with wide holes These holes can hold some other molecules of appropriate size interstitially.

Examination of liquid water near melting point of ice has shown that each water molecule has as its near neighbours about 4 or 5 other water molecules In this range of temperatures, liquid water is structurally close to ice. The breakdown of some hydrogen bonds during the melting of ice, makes the packing together of the new fragments somewhat closer but the open type structure still persists Thus, at the melting point, water is only slightly more dense than ice. As the temperature rises more hydrogen bonds are broken by thermal agitation and the packing of molecules becomes closer. The density of liquid water increases as temperature rises This tendency is offset by the expansion of water as temperature rises and the density of warer passes through a maximum near 277 K. The widespread hydrogen bonding in water is responsible for the requirement of a large heat of vaporization and a rather high boiling point. At the boiling point of water, kinetic motions of molecules are able to completely counteract the hydrogen bond forces and liquid water can change into free molecular vapour of water.

A complete description of water as a liquid has not so far been possible. A number of models have been proposed but none has been found to be entirely satisfactory The *cluster model* shown in Fig 3.13 is relatively simple and seems to be a nearly true representation. In this model, the liquid water is regarded as a mixture of clustered water molecules and single water molecules. The clusters are constantly breaking down and building up anew in rapid steps. Dimers, trimers and tetramers, all exist simultaneously as short lived intermediates between single molecules and molecular clusters.

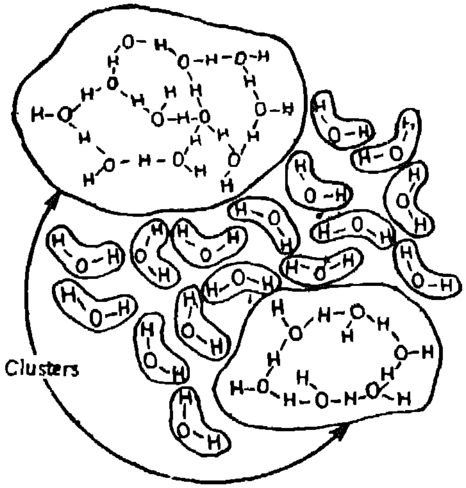


Fig 3 13 Cluster model of water

EXERCISES

3 1 Suggest explanations of the following statements :
- (i) Sodium chloride pieces are harder than sodium metal.
- (ii) Copper is ductile and malleable but brass is tenacious.
- (iii) Latent heat of fusion of solid carbon dioxide is much less than that of silicon dioxide
- (iv) Water has its maximum density near 277K
- (v) Ice floats on surface of water near the melting point

3.2 Draw a diagram to show structural difference between the three types of cubic crystals.

3 3 What are tetrahedral and octahedral holes in close packed stacks of spheres? What is the importance of these holes in crystals?

3.4 X-rays of wavelength equal to 0.154 nm give a first order diffraction from the surface of a crystal when the value of θ is 10 5° Calculate the distance between the planes in the crystal parallel to the surface examined.

3 5 Which of the following substances will conduct electricity in solid state and why ?
- (i) iodine, (ii) graphite, (iii) diamond, (iv) sodium chloride, (v) mercury.

3 6 A soft solid *A* melts slightly above 273 K, it is a poor conductor of heat and electricity. Solid *B* is quite hard and brittle It conducts neither electricity nor heat It can be melted about 1100 K and on melting forms a liquid which conducts electricity and undergoes electrolysis To which ones of the following classes of solids do *A* and *B* belong and why ?

(i) ionic (ii) metallic (iii) molecular (iv) covalent.

3 7 In the following statements fill the blanks choosing appropriate words from the list (1) crystal habits (ii) amorphous (iii) allotropes (iv) liquid crystals

(i) Monoclinic sulphur and rhombic sulphur are two——————of sulphur

(ii) A solid which melts over a broad range of temperatures is——————in nature

(iii) Crystals can be classified into seven basic——————

(iv) *If a crystalline pure solid on heating forms a turbid looking liquid which on further heating* forms a clear liquid, the first liquid form is known as——————

3 8 How is non-stoichiometric composition of compounds explained ?

3 9 What are point defects in crystals and how do they develop ?

3 10 How may defective crystals of non-metallic substances become conductors of electricity ?

3 11 List the advantages of alloy formation with examples.

3 12 List four abnormal properties of water How are these important for the role played by water in nature ?

UNIT 4

More About Chemical Energetics

The topic of chemical energetics was discussed earlier in Unit 6 of Part I The terms internal energy and enthalpy have been introduced there Here we shall try to develop a further understanding of energy changes in chemical reactions.

4.1 CONSERVATION OF ENERGY

Where does the heat evolved in a chemical reaction come from? When heat is absorbed in a chemical reaction, where does it go? In ordinary chemical changes energy can neither be created nor destroyed. If in a change some form of energy seems to disappear, it should reappear in some other form. For example, in the operation of an electric fan the consumed electrical energy takes the form of mechanical energy which moves the blades. When energy in the form of heat is absorbed by a body or a system, a part of it may go into changing the internal energy of the system and another part of it may be spent in doing some work. This may be mechanical work of expansion, electrical work, magnetic work, etc. Since energy cannot be destroyed nor created we can write

Heat energy absorbed by a system = Increase in internal energy of the system
+ Energy spent by the system in doing some work, where

Work done by the system = Expansion work + Non-expansion work.

The non-expansion part of work is usually directed into useful effects and is also called useful work. We can write the above information in a symbolic form as follows :

$$Q = \Delta E + W$$
$$= \Delta E + W_{\text{expansion}} + W_{\text{non-expansion}} \qquad \dots \quad (4.1)$$

where Q is the heat absorbed by the system, ΔE is the increase in its internal energy and W is the work done by the system on the surroundings.

Change in internal energy corresponds to a sort of bank balance. When we deposit some money in the bank and draw part of it for expenses, then

Bank balance = Bank deposit—Amount spent

or Bank deposit = Bank balance + Amount spent

The bank deposit corresponds to absorbed energy, Q, while amount spent corresponds to work done, W.

4.2 INTERNAL ENERGY

Internal energy of a substance is made up of a number of components, such as (i) energy of translation of molecules, (ii) rotational energy of molecules, (iii) vibrational energy of molecules, (iv) coulombic energy of electrons and nuclei in atoms, and (v) interaction energy for constituent particles in the substance

Molecules of a monoatomic gas possess only translational kinetic energy since vibrations and rotations are possible only with diatomic or polyatomic molecules. We have seen earlier that kinetic energy of such a gas is equal to $\frac{3}{2}$ RT per mole of gas*, so that

$$E_k = \frac{3}{2}RT \qquad \ldots\ \ldots (4.2)$$

4.3 ENTHALPY

A substance has to occupy a space in its surroundings according to its volume, V It does so against the compressing influence of prevailing pressure, P This gives a substance an additional energy, PV, of occupying space. The PV energy of a substance taken along with its internal energy, E, is called enthalpy, H, of the substance. This enthalpy is given by :

$$H = E + PV \qquad \ldots\ \ldots (4.3)$$

Enthalpy of a substance includes its internal energy and the PV work term.

If pressure is kept constant during a change, and no work other than expansion is done, we may write ·

$$\Delta H = \Delta E + P\Delta V \qquad \ldots\ldots (4.4)$$

And in terms of equation (4.1) we can write :

$$Q = \Delta E + P\Delta V \qquad \ldots\ldots (4.5)$$

Thus, for a change at constant pressure, the enthalpy change equals the heat absorbed by the substance.

Since, for monoatomic gas, all the internal energy is accounted for by the kinetic energy of its molecules, we can estimate enthalpy, H, per mole of such a gas at a temperature T as :

$$H = \frac{3}{2}RT + PV$$

Since PV = RT,

$$H = \frac{3}{2}RT + RT = \frac{5}{2}RT \qquad \ldots\ \ldots (4.)$$

By substituting the value of R and T in the above equation, the value of H is obtained.

4.4 DIRECTION OF A SPONTANEOUS CHEMICAL CHANGE

What is the criterion or the condition for a chemical reaction or any other change to occur spontaneously? We will try to answer this question in this section. For this purpose we shall examine some changes which are known to occur spontaneously.

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* *Chemistry Textbook*, Part I, p 80.

It is generally observed that a reaction like combustion proceeds spontaneously, releasing a large amount of heat. This would suggest that a spontaneous reaction will proceed in the direction of decrease in energy of the system. In other words, a reaction will proceed spontaneously if the products have a lower energy as compared to the reactants. However, this does not appear to be universally true as illustrated by the two cases given below

(i) Some endothermic changes proceed spontaneously. Heat is absorbed in them.

Examples

(a) Evaporation of water
(b) Dissolving of potassium nitrate in water

(ii) Some spontaneous chemical reactions do not go to completion.

Examples

(a) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$
(b) $CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$

Mixing of two chemically non-reacting gases is a spontaneous process as is observed in practice. It takes place without a change in temperature or energy. Consider two gases A and B in two containers connected by a narrow tube. The two initially separate gases are completely mixed up in the end. The final mixed up state of the gases is a state of maximum possible disorder (Fig. 4.1).

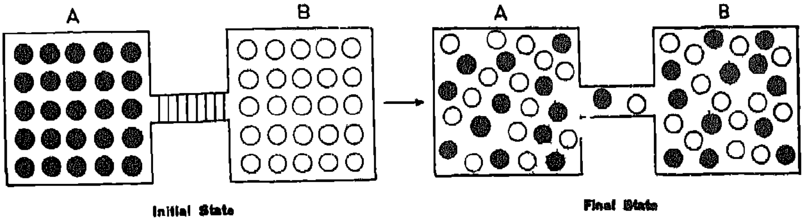


Fig. 4.1 Increase in disorder on mixing of two gases.

This example illustrates that a change may occur spontaneously, if it leads to increase in disorder even if no change takes place in energy of the system. It is an accepted fact that there is greater disorder in the gaseous state as compared to the liquid state. That is why evaporation of water is a spontaneous process although it is an endothermic process.

It follows that the direction of spontaneous occurrence of a process is dictated not only by the direction in which energy is lowered but also by the direction in which disorder increases. An endothermic process can occur spontaneously provided the extent of disorder outweighs the influence due to energy absorption. Is there any measure for disorder in a substance?

4.5 ENTROPY

There is a property of substances called entropy which measures the disorder in them. It is denoted by S. The change in entropy of the system, $S_{\text{final}} - S_{\text{initial}}$ is denoted by ΔS It has been observed that in reversible processes taking place under equilibrium conditions

$$\Delta S = \frac{Q}{T} = \frac{\Delta E + P\Delta V}{T} \quad \ldots\ldots (4.7)$$

and for irreversible or spontaneous processes,

$$\Delta S > Q/T$$

$$\text{or } \Delta S > \frac{\Delta E + P\Delta V}{T}$$

$$\text{or } \Delta S > 0 \quad \ldots\ldots (4.8)$$

Thus, in naturally occurring changes a system tends to alter in such a way that the entropy of the system increases. In other words, *processes occur spontaneously in the direction of increasing entropy.*

In order to correlate entropy and disorder we shall consider the processes of fusion and vaporization in the next section.

4.6 ENTROPY OF FUSION

The change in entropy when ice melts is given by

$$S_l - S_s = \Delta S_{fus} = \frac{\Delta H_{fus}}{T_f} \quad \ldots\ldots (4.9)$$

where S_l is the entropy per mole of liquid water, S_s the entropy per mole of solid ice (each at the melting point of ice), ΔH_{fus} the enthalpy of fusion, and T_f the fusion temperature of ice. Since ΔH_{fus} for melting of ice is 6025 J mol^{-1} and T_f is 273K,

$$\Delta S_{fus} = \frac{6025\text{J mol}^{-1}}{273\text{K}} = 22.1 \text{ J K}^{-1} \text{ mol}^{-1}$$

The S.I. unit of entropy is joules per kelvin*. Since ΔH_{fus} is positive, it follows that ΔS_{fus} is positive and, hence, $S_l > S_s$.

The liquid state is a state of greater disorder than the solid state. Solids are characterized by ordered arrangement of molecular or atomic species in the crystal** whereas in liquids there is greater disorder. Thus, it is justified to believe that entropy is a measure of randomness or disorder.

We will take another example to support the above point. The entropy of vaporization, $S_g - S_l = \Delta S_{vap}$ is given by:

$$\Delta S_{vap} = \frac{\Delta H_{vap}}{T_b} \quad \ldots\ldots (4.10)$$

---

*Earlier, entropy was expressed in units of calories per degree, i.e. 1 calorie per degree was called 1 entropy unit (abbreviated to e.u.).

***Chemistry Textbook*, Part I, Unit V, p. 73.

where ΔH_{vap} is the enthalpy of vaporization per mole and T_b the boiling point in kelvins. For diethyl ether, $\Delta H_{vap} = 27.2$ kJ mol^{-1} and $T_b = 308$ K. Hence,

$$\Delta S_{vap} = \frac{27.2 \text{ kJ mol}^{-1}}{308\text{K}} = .0883 \text{ kJK}^{-1}\text{mol}^{-1} = 88.3 \text{ JK}^{-1} \text{ mol}^{-1}$$

Here again, ΔS_{vap} is positive suggesting that

$$S_g > S_l \qquad \text{.........(4.11)}$$

It is known that the gaseous state is characterized by a far greater disorder than the liquid state where a certain degree of order persists. Here again, entropy can be taken as a measure of disorder, randomness or chaos in the system.

4.7 FREE ENERGY

For a further understanding of spontaniety in changes, we introduce here a new function called free energy of the stsyem. It is denoted by the symbol G and is also known as Gibb's free energy. Relations of G to the functions E, H, S and T are given by the following equations :

$$\begin{aligned} G &= H - TS \qquad \text{........(4.12)} \\ &= E + PV - TS \end{aligned}$$

$$\text{and } \Delta G = \Delta H - \Delta (TS) = \Delta E + \Delta (PV) - \Delta (TS) \qquad \text{........(4.13)}$$

For a change under constant pressure and temperature conditions, the term $\Delta(P V)$ can be replaced by $P \Delta V$ and the term $\Delta(TS)$ by $T \Delta S$. We can then write :

$$\begin{aligned} (\Delta G)_{T,P} &= \Delta E + P\Delta V - T\Delta S \\ &= \Delta H - T\Delta S \qquad \text{.......(4.14)} \end{aligned}$$

For a spontaneous change, the most helpful conditions are an increase in entropy and a decrease in energy or enthalpy of the system. Under these conditions, ΔH is negative and ΔS is positive and, according to Eq. 4.14, ΔG should be negative. Thus, *in a spontaneous change, free energy of the system always decreases.* For a spontaneous change :

$$(\Delta G)_{T,P} < 0 \qquad \text{..... (4.15)}$$

and under equilibrium conditions

$$(\Delta G)_{T,P} = 0 \qquad \text{.........(4.16)}$$

4.8 PHYSICAL SIGNIFICANCE OF FREE ENERGY

The relationship between heat absorbed by a system, Q, the change in its internal energy, ΔE, and the work done by the system, is given (vide Eq. 4.1) by :

$$Q = \Delta E + W_{\text{expansion}} + W_{\text{non-expansion}}$$

The expansion work under constant pressure condition is given by $P\Delta V$. Hence,

$$\begin{aligned} Q &= \Delta E + P\Delta V + W_{\text{non-expansion}} \\ &= \Delta H + W_{\text{non-expansion}} \qquad \text{........(4.17)} \end{aligned}$$

When a change is carried out reversibly at a temperature T,

$$\Delta S = \frac{Q}{T} \qquad \text{(vide Eq. 4.7)}$$

$$\text{or } Q = T\Delta S \qquad \ldots\ldots (4.18)$$

Substituting for Q from Eq. 4.18 into Eq. 4.17 gives

$$T\Delta S = \Delta H + W_{\text{non-expansion}}$$

$$\text{or } \Delta H - T\Delta S = -W_{\text{non-expansion}} \qquad \ldots\ldots\ldots (4.19)$$

Also, for a change taking place under a condition of constant temperature and pressure,

$$(\Delta G)_{T,P} = \Delta H - T\Delta S \qquad \text{(vide Eq. 4.14)}$$

Comparing Eqs. 4.14 and 4.19, we have

$$(\Delta G)_{T,P} = -W_{\text{non-expansion}} \qquad \ldots\ldots\ldots (4.20)$$

For most changes the work of expansion cannot be converted to other useful work, while the non-expansion work is convertible to useful work. Eq. 4.14 may be rearranged to :

$$\Delta H = \Delta G + T\Delta S \qquad \ldots\ldots (4.21)$$

Thus, the energy change in a system under a constant pressure condition, ΔH, is equivalent to two types of work, the non-expansion or useful work (ΔG) and the work of expansion of the system or the non-available work ($T\Delta S$). Rearranging Eq. 4.20, we have :

$$W_{\text{non-expansion}} = -(\Delta G)_{T,P}$$

Thus, the decrease in free energy of the system during any change, ΔG, is a measure of the useful or net work derived during the change, we may generalize to say that the free energy, G, of a system is a measure of its capacity to do useful work. It is a part of the energy of the system which is free for conversion to useful work and is, therefore, called *free energy*.

If in a process the enthalpy increase be ΔH and free energy increase be ΔG, the *efficiency* of the process to do useful work would be $\Delta G/\Delta H$, or

$$\text{Efficiency} = \frac{\Delta G}{\Delta H} \quad \frac{\text{Useful work obtainable from the system}}{\text{Total energy absorbed by the system}}$$

Work efficiencies of some of the power devices are given below.

Device	*Efficiency* (%)
Heat engine	30
Electricity to light	40
Dry cell	70
Fuel cell	100

4.9 CONDITIONS FOR EQUILIBRIUM AND SPONTANEOUS CHANGES

The conditions for equilibrium and spontaneous occurrence of processes are summarized in Table 4.1.

TABLE 4.1

Conditions for Equilibrium and Spontaneous Changes

Equilibrium	Spontaneous change
$(dS)_{E,V}=0$	$(dS)_{E,V}>0$
$(dG)_{T,P}=0$	$(dG)_{T,P}<0$

Change in Gibb's free energy is given by : $\triangle G=\triangle H-T\triangle S$ (vide Eq. 4.14). Here, the term $\triangle H$ stands for energy change and the term $T\triangle S$ stands for change in extent of order existing in the system. The energy term balances the disorder term at equilibrium. In a reversible chemical change, equilibrium state is reached when $\triangle H$ balances $T\triangle S$. Then, $\triangle G$ for conversion in either direction will be zero (Fig. 4.2).

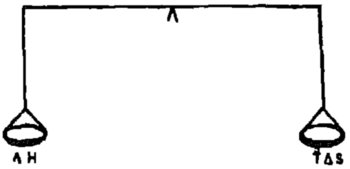


Fig. 4.2. Equilibrium balance.

4.10 PREDICTION ABOUT A REACTION

Only those processes can occur spontaneously for which free energy change is negative. On the basis of this statement and Eq. 4.14, $\triangle G=\triangle H-T\triangle S$, following conclusions can be drawn :

(i) If, for a particular process, $\triangle H$ is negative and $\triangle S$ is positive, $\triangle G$ will certainly be negative. Thus, a reaction or a process, for which entropy of the products is greater and the energy is less than that for reactants, would occur spontaneously.

(ii) If both $\triangle H$ and $\triangle S$ are positive, the process can occur spontaneously only when : $T\triangle S$ is greater than $\triangle H$, so that $\triangle G$ will be negative.

(iii) If $\triangle H$ is positive while $\triangle S$ is negative, $\triangle G$ will be positive and the reaction or the process cannot occur. These conclusions are summarized in Table 4.2.

TABLE 4.2

Conditions for Spontaneity in a Reaction

Sign of $\triangle H$	Sign of $\triangle S$	Occurrence of reaction
+ ; increases	+ ; increases	Reaction occurs only if $T\triangle S>\triangle H$
− ; decreases	− , decreases	Reaction occurs only if $\triangle H>T\triangle S$
+ ; increases	− , decreases	Occurrence impossible
− ; decreases	+ , increases	Reaction occurs

4.11 PROBABILITY OF A CHANGE AND TEMPERATURE

We can use Eq 4 14 for predicting whether a change can occur at a particular temperature. To illustrate this point, consider the case of vaporization of water, i.e. the process .

$H_2O(l) \rightarrow H_2O(g)$

at 1 atm pressure, ΔH for this process is 40 63 kJ mol^{-1} and ΔS is 108 8 JK^{-1} mol^{-1} Hence,

$$\Delta G = 40.63 \times 10^3 \text{ J mol}^{-1} - T \text{ K} \times 108\ 8 \text{ JK}^{-1} \text{ mol}^{-1}$$

The equilibrium condition under 1 atm external pressure is that of boiling water At this temperature the change will occur reversibly and ΔG will be zero The temperature at which $\Delta G = 0$ is, therefore, given by

$$T = \frac{40.63 \times 10^3}{108\ 8} = 373.4 \text{ K}$$

This result is very close to the boiling point observed for water under 1 atm pressure Now, when T is above 373 4K, ΔG is less than zero and the vaporization will occur spontaneously and continuously

4.12 PREDICTING THE SIGN FOR ΔH

We can qualitatively predict the sign of ΔH for a change on the following lines

(i) Reactions in which bonds are formed are invariably exothermic. The reaction,

$I(g) + I(g) \rightarrow I_2(g)$

is exothermic, since an I — I bond is formed

(ii) Bonds between atoms of different elements are usually stronger than bonds between atoms of the same element Hence, the enthalpy change for a reaction leading to the formation of bonds between unlike atoms starting with homoatomic molecules would be negative Thus, for the reaction

$H{-}H(g) + Cl{-}Cl(g) \rightarrow 2H{-}Cl(g)$

ΔH should be negative and so it is an exothermic reaction

(iii) If more bonds are broken than formed in a reaction, it will usually be accompanied by absorption of heat and ΔH will be positive Thus, the following reaction would be expected to be endothermic

$CH_3CH_2OH(g) \rightarrow CH_2{=}CH_2(g) + H_2O(g)$

Calculation of actual ΔH can be made with the help of bond-energies. (*See* Part I, Sec. 6.8)

4 13 PREDICTING THE SIGN FOR ΔS

The sign of ΔS for a reaction is known from the difference between the entropies of the products and of the reactants, $S_{\text{products}} - S_{\text{reactants}}$ Prediction is possible in some cases such as the following:

(i) ΔS would be positive for a reaction where the number of molecules of products exceeds the number of molecules of reactants, as in the following reaction :

$2SO_3(g)$	$\rightarrow$	$2SO_2(g)+O_2(g)$
less number of molecules, less entropy		greater number of molecules, greater entropy

Here, two molecules of the reactant produce three molecules of the products.

(ii) ΔS would also be positive when a solid decomposes to give one or more gases amongst the products, as in the following case :

$MgCO_3(s)$	$\rightarrow$	$MgO(s) + CO_2(g)$
less entropy		greater entropy

(iii) ΔS would be positive when a solid melts or sublimes or when a liquid boils or evaporates in view of greater disorder in the molten and gaseous states.

EXERCISES

4.1 What do you mean by the law of conservation of energy ? Write a mathematical relationship between heat, internal energy and the work done by the system.

4.2 State whether each of the following will increase or decrease the total energy content of a system . (i) work done by the system, (ii) heat transferred to the surroundings, (iii) work done on the system, and (iv) against an external pressure.

4.3 Correlate entropy and disorder with the help of fusion and vaporization processes.

4.4 What do you understand by the term free energy ? What is its physical significance ?

4.5 Explain the following terms in brief :
  (i) Enthalpy
  (ii) Entropy
  (iii) Free energy

4.6 How will you predict the occurrence of a change at a particular temperature ? Explain it with the help of an example.

4.7 Calculate the change in E, H, S and G for the expansion of 10 moles of an ideal gas from 10 litres to 224 litres at 273K, expanding against an external pressure at 1 atm

4.8 What is the entropy change for the conversion of a mole of ice to water at 273 K, and 1 atm ?

4.9 Describe the conditions at which any or all of the followings may be zero: $Q, W, \Delta E, H, \Delta H, S, \Delta S$, and ΔG.

4.10 (a) Write an expression for the free energy change of a chemical reaction and discuss the significance of the expression.
(b) Show that the change in free energy is equal to the net work done.

4.11 Calculate the entropy change involved in the conversion of 1 mole of liquid water at 373 K to vapour at the same temperature. (Latent heat of vaporization, $\Delta H_{vap}=2.257$ kJ/g)

4.12 For the reaction, $Ag_2O(s) \rightleftharpoons 2Ag(s) + \frac{1}{2} O_2(g)$, calculate the temperature at which free energy change (ΔG) is equal to zero.
($\Delta H=+30.56$kJ and $\Delta S=+0.066$kJ at 1 atm pressure)
Predict also the nature of the reaction at this temperature and below it

UNIT 5

Kinetics of Chemical Reactions

You are now familiar with a number of organic and inorganic reactions. During laboratory work you would have observed that certain reactions are fast while others are slow In this unit, we shall consider : (i) How we can measure the speed of a reaction ? (ii) How the speed of a reaction is related to concentrations of the reactants and products ? and (iii) Other factors on which the speed of a reaction depends.

This information will enable us to predict the rates of reactions and to control them by altering the parameters on which reaction rates depend.

5 1 SLOW AND FAST REACTIONS

Rusting of iron and burning of fuel are both oxidation reactions. The first is a typical slow reaction while the second is an example of a fast reaction. The reaction between dry hydrogen and chlorine gases in the absence of light is an immeasurably slow reaction, but it becomes explosive when a trace of sodium vapour is introduced. A rough idea about speeds of reactions can be obtained by knowing the times of completion of reactions Thus, at room temperature the reaction :

$$2NO_2+O_3 \rightarrow N_2O_5+O_2$$

is completed within 1/10 of a second, whereas the completion of the reaction

$$H^+ + OH^- \rightarrow H_2O$$

takes less than a millisecond.

5.2 RATES OF REACTION

The first major question is how to define the rate of a reaction.

The rate of a reaction like A→B could be set as the amount of A transformed or the amount of B produced during a time interval Δt. The amount of A transformed will depend on the initial amount of reactant, and the length of time interval chosen. Therefore, it is found to be more convenient to specify the rate of a reaction in terms of *concentration change per unit time*. Accordingly :

$$\text{Rate of reaction} = -\frac{\Delta[A]}{\Delta t} = +\frac{\Delta[B]}{\Delta t} \qquad \text{......} \ (5.1)$$

Minus sign in the above expression is used to indicate a decrease in concentration with increase in time. The use of square brackets around the formula of a substance stands for its concentration. This way of defining rate of a reaction would have been right if the concentrations of A and B changed linearly as shown in Fig 5.1.

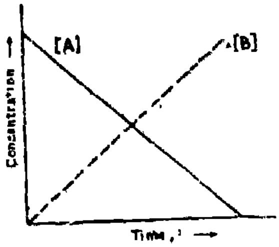


Fig. 5.1 Hypothetical variation of A and B with time during reaction

Except in a few cases, the concentrations of reactants and products in chemical reactions do not change linearly with time. The type of variation usually observed is as shown in Fig. 5.2 for decomposition of N_2O_5 in CCl_4 medium, viz $2N_2O_5 = 2N_2O_4 + O_2$

The experimental values of concentrations of N_2O_5 and O_2 at various times are recorded in Table 5.1

TABLE 5.1

Decomposition of N_2O_5 in CCl_4 at 318K

Time (sec)	$[O_2]$ (moles/litres)	$[N_2O_5]$ (moles/litres)	k (sec^{-1} x 10^4)
0	0.00	5.53	—
82	0.14	5.04	6.97
162	0.27	4.78	6.67
409	0.62	4.06	6.37
604	0.96	3.36	6.37
1129	1.44	2.37	6.67
1721	1.83	1.57	6.95
1929	1.94	1.36	6.99
3399	2.34	0.53	6.99

It is apparent from Figs. 5.2 (a) and 5.2 (b) that since the slopes of the curves change with time, it is not possible to fix the reaction rate by $-\frac{\Delta[N_2O_5]}{\Delta t}$ or $\frac{\Delta[O_2]}{\Delta t}$ over finite time intervals. We can only talk sensibly of a reaction rate over a small time interval during which the slope of the line and, hence, the rate of reaction is almost constant. Mathematically, such rates are denoted by $-\frac{d[N_2O_5]}{dt}$ and $\frac{d[O_2]}{dt}$, where $d[N_2O_5]$ or $d[O_2]$ denotes a very small change in concentration in a very small time interval dt. To give unique values of reaction rates, the rates as defined above

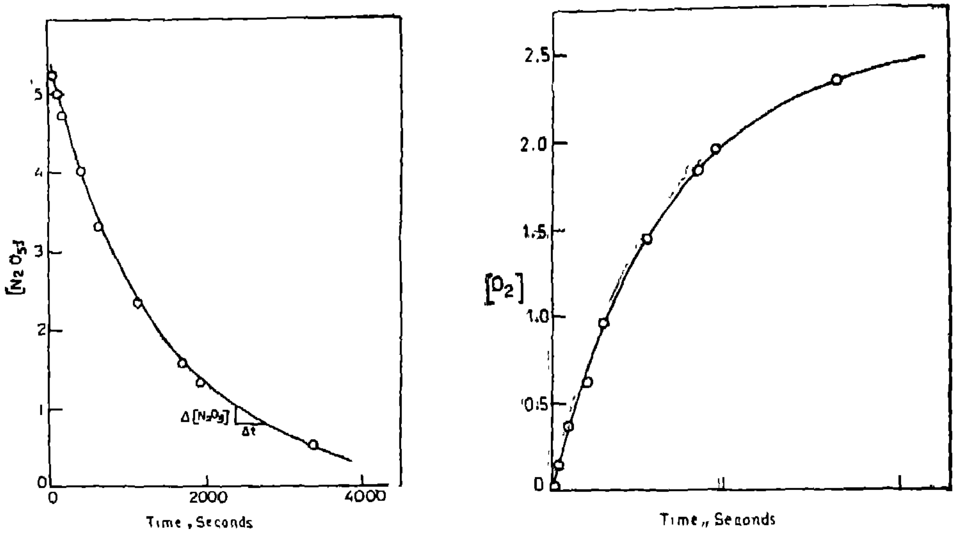


Fig 5 2 (a) Variation of $[N_2O_5]$ with time (b) Variation of $[O_2]$ with time

are further divided by the index numbers of molecules in the stoichiometric equation for the reaction. Thus, for the decomposition of N_2O_5, we find that :

$$-\frac{d[N_2O_5]}{dt} = \frac{d[N_2O_4]}{dt} = \frac{2\,d[O_2]}{dt} \qquad \text{........(5.2)}$$

Hence for having equal or unique value of the reaction rate independent of the concentration term chosen, we should define the rate of this reaction (vide Eq. 5.2) as :

$$\text{Rate of reaction} = -\tfrac{1}{2}\,\frac{d[N_2O_5]}{dt}$$

$$= \tfrac{1}{2}\,\frac{d[N_2O_4]}{dt}$$

$$= \frac{d[O_2]}{dt} \qquad \text{... ....(5.3)}$$

A very general symbol used for rates of reactions is $\frac{dx}{dt}$, where x is decrease in concentration of reactant or one of the reactants due to reaction upto time t.

5.3 DEPENDENCE OF REACTION RATE ON CONCENTRATION

Let us again consider Fig. 5 2 (a). The slope of the curve at any instant would be d $[N_2O_5]/dt$ or d $[O_2]/dt$, which would be a measure of the reaction rate at that instant. Whereas the slope is constant in Fig. 5.1, it is not so in Fig. 5.2 (a). In fact, in the latter case, the value of slope progressively decreases as the concentration of N_2O_5 decreases. This shows that the rate of reaction depends on concentration of the reactant

N_2O_5. Fig. 5.2 (a) suggests that log$[N_2O_5]$ or ln$[N_2O_5]$ values would be proportional to time. In order to test it, we have plotted log $[N_2O_5]$ against time (t) in Fig. 5.3, where the expected straight line is obtained The slope of this straight line is constant and negative. Thus, we may write :

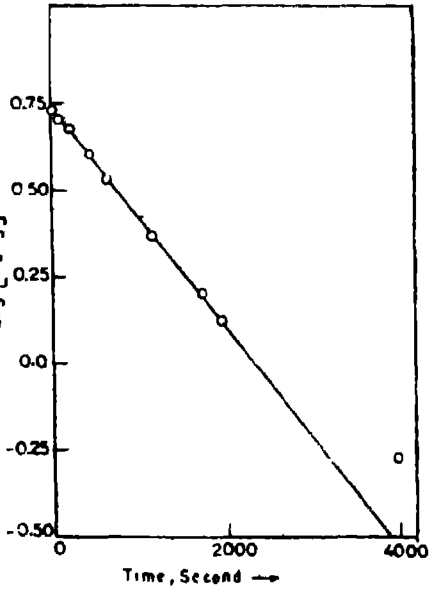


Fig. 5.3 Plot of log $[N_2O_5]$ against time, t.

$$\frac{d\ \ln[N_2O_5]}{dt} = \text{constant} = k \qquad \text{.. .....(5.4)}$$

Mathematically, $d \ln x = \frac{1}{x} dx$. Hence,

$$d\ \ln[N_2O_5] = \frac{d[N_2O_5]}{[N_2O_5]}$$

and Eq. 5.4 takes the form :

$$-\frac{1}{[N_2O_5]} \cdot \frac{d[N_2O_5]}{dt} = k$$

or $$-\frac{d[N_2O_5]}{dt} = k\ [N_2O_5] \qquad \text{... .. (5.5)}$$

Alternatively, $\frac{dx}{dt} = k[N_2O_5]$

From this it follows that the rate of reaction is proportional to the first power of concentration in the case of decomposition of N_2O_5 A relationship as shown in Eq. 5.5

is called *rate equation* or *rate law* for the reaction To be more exact, it is the differential form of the rate law

The rate laws for most of the reactions are not as simple as Eq 5.5. The rate of saponification of ethyl acetate,

$$CH_3COOC_2H_5 + OH^- \longrightarrow CH_3COO^- + C_2H_5OH$$

is described by the rate equation :

$$\frac{d[CH_3COOC_2H_5]}{dt} = k\,[CH_3COOC_2H_5][OH^-]$$

Similarly, rate equation for the reaction between nitric oxide and oxygen, $2NO + O_2 \rightarrow 2NO_2$, is given by .

$$\frac{d[NO]}{dt} = k\,[NO]^2[O_2]$$

For any general reaction, $aA + dD \rightarrow cC$, we can write :

$$-\frac{d[A]}{dt} = k\,[A]^m\,[D]^n \qquad \text{..} \quad (5.6)$$

where *m* and *n* are constant numbers for a reaction and may be integers or fractions

The constant *m* is said to be the order of reaction with respect to reactant A and *n* the order of reaction with respect to D. The sum ($m+n$) denotes the total order of the reaction. Thus, saponification of ethyl acetate is a *second* order reaction, while the combination of NO and O_2 is a *third* order reaction.

In the rate law equations the factor *k* is given a number of names, the most common being *rate constant* for the reaction and *specific reaction rate*. Numerically, it equals the rate of the reaction when all the involved concentration terms equal unity

For the general first order reaction, A→B, if *a* stands for the initial concentration of A and (a-x) for the concentration of A at any time *t*, following Eq 5.5, we can write :

$$-\frac{d(a-x)}{dt} = k\,(a-x) \qquad \ldots(5.7)$$

$$\text{Also } \frac{dx}{dt} = k\,(a-x) \qquad .(5.8)$$

$$\text{or } \frac{dx}{(a-x)} = k\,dt,$$

which on integration yields:

$$-\ln\,(a-x) = kt + \text{constant I} \qquad \ldots(5.9)$$

We know that when $t=0$, $x=0$. Substitution of this condition into Eq. 5.9 gives a value of $-\ln a$ for the integration constant I On making this substitution, Eq. 5.9 can be written as :

$$-\ln\,(a-x) = kt - \ln a$$

This may be arranged as

$$\ln \frac{a}{a-x} = kt \qquad \dots(5.10)$$

$$\text{or} \quad k = \frac{1}{t} \ln \frac{a}{a-x} \qquad (5.11)$$

In terms of common logarithms Eq 5.10 would become

$$2.303 \log \frac{a}{a-x} = kt \qquad (5.12)$$

Eqs. 5.11 and 5.12 are two expressions for the integrated rate law relating to first order reactions The reaction rate in such reactions is proportional to the first power of concentration of the reactant (Eq. 5.8) Radioactive decays are first order processes since the rate of any decay at all stages is proportional to the number of undisintegrated nuclei present. Values of *k* calculated for N_2O_5 decomposition using Eq. 5.12 are shown in the fourth column of Table 5.1. The nearly constant value of *k* confirms that decomposition of N_2O_5 is a first order reaction.

Integrated rate laws can also be developed for reactions of orders higher than one, but they are not being taken up in this course.

Example 5.1

Experiments on the catalytic decomposition of hydrogen peroxide by colloidal platinum gave the following results :

Time (min)	*$KMnO_4$ in ml to decompose 20 ml of H_2O_2*
0	18.0
5	14.0
10	10.9
20	6.6

Show from the data that the catalytic decomposition is a first order reaction and determine the value of the rate constant.

Solution

Here, *a* ∝ titre value at zero time (*t* = 0), i.e. 18.0 mL and (*a* − *x*) ∝ titre value at time *t* Substituting the values of *a* and (*a* − *x*) and *t* in the first order rate equation we get :

t (min)	a	(a−x)	$k = \frac{2.303}{t} \log \frac{a}{a-x}$
(i) 5	18.0	14.0	$k = \frac{2.303}{5} \log \frac{18}{14} = 0.05020$
(ii) 10	18.0	10.9	$k = \frac{2.303}{10} \log \frac{18}{10.9} = 0.05018$
(iii) 20	18.0	6.6	$k = \frac{2.303}{20} \log \frac{18}{6.6} = 0.05018$

As the values of k are same, the reaction is of first order.

The value of the rate constant is 0.05019 min^{-1} or 8.36×10^{-3} sec^{-1}

5.4 HALF LIFE OF A REACTION

The time in which half of a reaction is completed (or half the reacting quantity of any of its reactants is consumed in the reaction) is called half life period or simply half life of the reaction. From Eq 5.11, we can determine the half life period for a first order reaction. At the end of the half life period, the initial concentration, a, will be reduced to $a/2$. Then, x and $(a\text{-}x)$ will both be equal to $a/2$. Let the half change time be denoted by $t_{\frac{1}{2}}$ On the basis of Eq. 5.10, we can write ·

$$t_{\frac{1}{2}} = \frac{1}{k} \cdot \ln\frac{a}{a/2} = \frac{\ln 2}{k}$$

$$= \frac{2.303 \log 2}{k} = \frac{2.303 \times 0.3010}{k} = \frac{0.693}{k} \qquad \ldots\ldots (5.13)$$

Since, the initial concentration of the reactant does not occur on the right hand side of Eq. 5.13, it follows that for a first order reaction, **time for half change is independent of the initial concentration of reactant.**

We can, in the same manner, estimate the time for any other fraction of reaction such as one-third change. Substituting a/3 for x in Eq 5.10, we get .

$$t_{\frac{1}{3}} = \frac{1}{k} \ln\frac{3}{2} = \frac{2.303}{k} \log 1.5 = \frac{0.405}{k} \qquad \ldots \qquad (5.14)$$

The time for one-third change is also independent of initial concentration of reactants and so is the time for any other fractional change for a first order reaction.

Example 5.2

The reaction, $SO_2Cl_2 \rightarrow SO_2 + Cl_2$, is a first order reaction. The time required to decompose SO_2Cl_2 by heating to 50% of its initial amount is 60 minutes. Calculate the rate constant of the reaction at 590K.

Solution

Half life time of a first order reaction $= \frac{0.693}{k}$, where k is the rate constant.

$$k = \frac{0.693}{t_{\frac{1}{2}}}$$

$$= \frac{0.693}{60 \times 60} \text{sec}^{-1}$$

$$= 3.2 \times 10^{-5} \text{ sec}^{-1}$$

The rate constant of the reaction is 3.2×10^{-5} sec^{-1}

5.5 UNITS OF REACTION RATES AND RATE CONSTANTS

Rates of reactions denote the change in concentration of a specified reactant or product or reaction per unit time. Hence, rates of reactions are expressed in terms of concentration units divided by time units. If the concentration be expressed in moles/litre and time in seconds, the unit for the rate of a reaction will be mol litre^{-1} sec^{-1}.

The units for a first order rate constant can be determined on the basis of Eq. 5.11. Since ln $a/(a-x)$ is a dimensionless pure number (because both a and $(a-x)$ would be in the same concentration units), units for k would be sec^{-1}, min^{-1}, etc., depending on how time is expressed. However, the units of k for second and third order reactions would be different. These are indicated in Table 5.2.

TABLE 5.2

Units of Reaction Rate Constants

Order of reaction	Typical rate law (differential)	(integrated)	Units for k
First	$-\frac{d[A]}{dt}=k[A]$	$k=\frac{1}{[A]}\frac{d[A]}{dt}$	sec^{-1}
Second	$-\frac{d[A]}{dt}=k[A]^2$	$k=\frac{1}{[A]^2}\cdot\frac{d[A]}{dt}$	litre mol^{-1} sec^{-1}
Third	$-\frac{d[A]}{dt}=k[A]^3$	$k=\frac{1}{[A]^3}\frac{d[A]}{dt}$	litre^2 mol^{-2} sec^{-1}

5.6 ORDER AND MOLECULARITY OF A REACTION

The *molecularity* of a reaction is the number of molecules of the reactants taking part in a single actual step of the reaction. Stoichiometric equation for a reaction indicates the net change in the reaction. It may have arisen from a combination of a number of individual reaction steps. Thus, it will not be reasonable to use a stoichiometric equation for deciding the molecularity of a reaction. When one molecule of the reactant is involved in a step of the reaction, such a reaction is called unimolecular reaction. On the other hand, when two molecules take part in a step of the reaction, such a reaction is called a bimolecular reaction. Most reaction steps are bimolecular, some are unimolecular. Termolecular reaction steps are rare. Stoichiometric equations involving three or more molecules are, however, quite common.

Information about the order of a reaction is obtained from its rate equation, and rate equations are based on experimental data. They are independent of, and often unrelated to, reaction stoichiometries. Order of a reaction is equal to the sum of the indices to which the concentration terms are raised in the rate equation for the reaction. Eq 5.5 indicates that the decomposition of N_2O_5 is a first order reaction. It should be noted that when stoichiometric number of molecules of reactants in a reaction is different from its order, the reaction occurs in steps, which cannot be suggested by the stoichiometric equation for the reaction. A knowledge of steps involved in a reaction is called *mechanism of the reaction.*

5.7 FACTORS AFFECTING RATES OF REACTIONS

The rate of a reaction is influenced by : (i) concentrations of reactants, (ii) temperature, (iii) presence of a catalyst, and (iv) exposure to radiation and radiation intensity. A qualitative discussion of these influences follows.

5.8 REACTION RATES AND CONCENTRATION CHANGES

Consider Eq. 5.6 :

$$-\frac{d[A]}{dt}=k\ [A]^m\ [D]^n$$

It is obvious from this equation that when the concentration factor [A] or [D] increases, the rate of reaction will increase proportionally. How it happens would become clear if we consider a reaction in gas phase. The reactant molecules move about with great speeds. During their movements they frequently collide with each other and such collisions are the most important requirement for a chemical change. Greater the concentrations of the reactant molecules, greater would be the number of reactant molecules per litre and hence greater would be the number of collisions between molecules per litre per second. Consequently, the rate of a reaction would become more when the concentration of any of its reactants is increased

5.9 REACTION RATES AND TEMPERATURE CHANGES

With an increase in temperature of reactants from 298 to 308 K, molecular velocities increase by about 2% and, hence, the collisions between molecules would also increase by 2%. This would increase the reaction rate, but only to a small extent. Actually, temperature changes influence rates of reactions much more and more steeply than concentration changes. Roughly, the rates of reactions and their rate constants become double when the temperature is increased by ten degrees.

Rate constants for the gas phase decomposition of nitrogen pentoxide at different temperatures are given in Table 5.3.

TABLE 5.3

Rate Constants for Gas Phase Decomposition of N_2O_5 at Different Temperatures

T(K)	$\frac{1}{T}\times 10^3$	$k \times 10^5$ (sec^{-1})	log k
338	2.959	487.0	−2.313
328	3.048	150.0	−2.824
318	3.145	49.8	−3.303
308	3.247	13.5	−3 871
298	3.357	3.56	−4.461
273	3.663	0 0787	−6.104

The rate constant at 273K is 7.87×10^{-7} sec^{-1}, while at 298K its value is 3.46×10^{-5} sec^{-1}. Thus, for a rise of 25°, the rate constant is increased by about 43 times. It is obvious from Table 5.3, that the increase in the value of *k* with rise in temperature is very rapid and this increase cannot be explained on the basis of an increase in the number of collisions on increasing the temperature It appears to be an exponential increase shown by the *k* versus *T* plot [Fig. 5.4 (a)].

In order to determine a quantitative relationship between rate constants and temperature, we plot log *k* versus $1/T$ [Fig. 5.4 (b)].

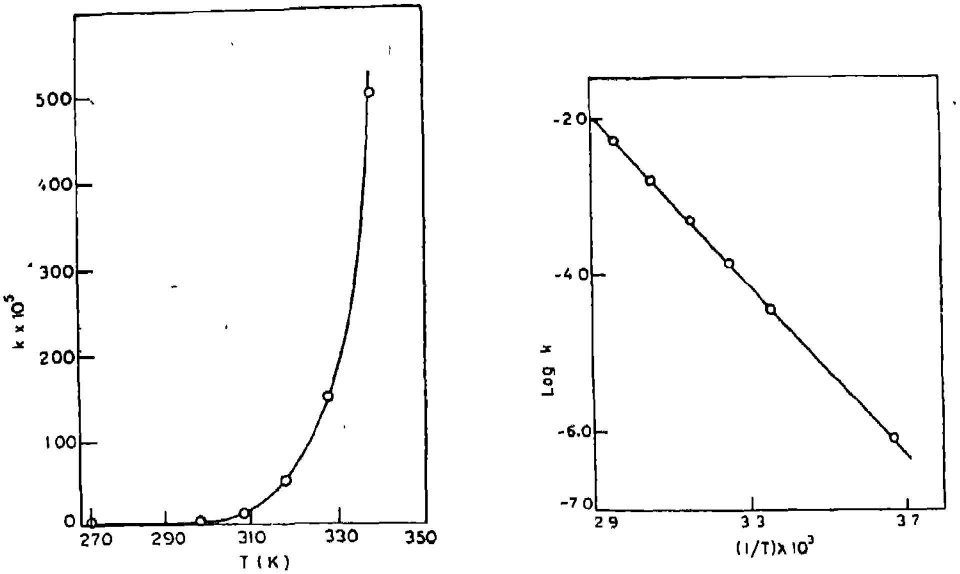


Fig 5.4 (a) Variation of k with temperature (vide Table 5.3). (b) Plot of k versus reciprocal of kelvin temperature.

Since a straight line is obtained in this graph, we can write :

$$\log k = -B/T + \text{constant } A' \qquad \ldots\ldots(5.15)$$

Arrhenius found that when natural logarithms of k or ln k, values are plotted against $1/T$ values, the slope constant B in Eq. 5.15 becomes equal to E/R, where R is the familiar gas constant and E an energy factor. The added or intercept constant in Eq. 5.15 can then be set in a logarithmic form, say ln A. Thus, Eq. 5.15 may be written as :

$$\ln k = \ln A - \frac{E}{RT}$$

$$\text{or } k = A\, e^{-E/RT} \qquad \ldots\ldots\ldots(5.16)$$

Eq. 5.16 is called the Arrhenius equation, and the factor A is related to the number of binary molecular collisions per second per litre and is called the frequency factor of the Arrhenius equation. The exponential energy factor E denotes the minimum energy that reacting molecules must possess individually on per mole basis, before their collisions can result into a chemical change. This minimum molecular energy is called the *activation energy* of the reaction and is sometimes assigned the symbol E_a. The activation energy requirement immediately explains two things :

(i) Why all molecular collisions are not effective for chemical change ?

(ii) Why reaction rates are very highly sensitive to temperature changes ?

Fig 5.5 shows schematically how the molecules in a gas are distributed energy-wise.

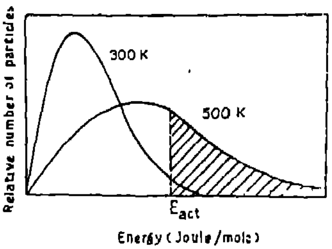


Fig 5 5 Distribution of molecules according to energy (dotted line separates optimum energy region)

We suppose that all molecules possessing velocity greater than the threshold velocity and possessing a minimum energy of 1/2 mc^2 per molecule (where m is the mass of the molecule) would be successful in bringing about a chemical transformation The *threshold energy* is equivalent to factor E of Eq. 5.16. Again, from the kinetic theory of gases, it is found that the fraction of molecules having energy lying in the range E to $E + dE$ is just $e^{-E/RT}$. Hence, if total binary collisions in a gas per second per litre, or the frequency of collision, be Z,

$$\text{Effective collision} = Ze^{-E/RT} \qquad \ldots\ldots(5.17)$$

$$\text{Hence, rate of reaction} = Ze^{-E/RT} \qquad \ldots\ldots(5.18)$$

For a bimolecular reaction, $A + B \rightarrow C$

$$\text{Rate of reaction} = k[A]\,[B] \qquad \ldots\ldots(5\ 19)$$

$$k[A][B] = Z.e^{-E/RT}$$

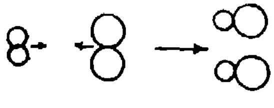
$$\text{or } k = \frac{Z}{[A]\,[B]}\,e^{-E/RT} \qquad \ldots(5\ 20)$$

which is similar to Arrhenius equation (Eq 5 16) with $A = Z/[A]\ [B]$. As the energy-wise distribution of molecules in a gas is an exponential function of temperature, a small increase in temperature rapidly increases the number of molecules with energies E and above This explains why the rates of reactions increase steeply when temperature increases.

5.10 ORIENTATION OF MOLECULES AND EFFECTIVE COLLISION

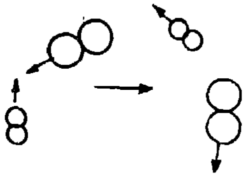
It has been found in many cases that the predicted values of the rates on the basis of Eq. 5 18 are much higher as compared to experimentally observed values. This is due to the fact that a large percentage of collisions become ineffective if the colliding molecules are not in proper orientation at the actual time of collision (Fig. 5.6)

Consider the reaction, $CH_3I + K \rightarrow CH_3 + KI$, between beams of molecules of methyl iodide and potassium. It has been experimentally observed that when K atoms hit the iodide end of the molecule, the reaction rate is much faster than when K atoms strike the methyl end of the molecule. Thus, *in order to have an effective collision, the reactant molecules must be in proper orientation at the time of colliding*. In order to take this factor into account, Eq. 5.18 is written as .



Effective collision

(a)



Ineffective collision

(b)

Fig. 5 6 Collision between molecules resulting in chemical change

Rate of reaction $= p.Z.\ e^{-E/RT}$ ....(5.21)
where p is called the probability or steric factor

5.11 ENERGY BARRIER AND ACTIVATED COMPLEX

We shall further explore the significance of energy of activation. Let us consider the reaction, $H_2 + I_2 \rightarrow 2HI$, and try to imagine its course During collision, H_2 and I_2 molecules would come near each other and, prior to the formation of HI, the bonds between atoms in hydrogen and iodine molecules would be loosened due to molecular interactions and an intermediate complex will be formed as shown in Fig 5.7.

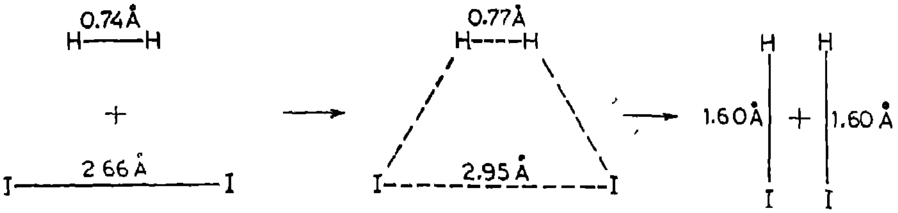


Fig 5.7 Hydrogen-iodine activated complex

In the formation of this complex, the H.. . .H and I .....I distances will be longer than the bond lengths in hydrogen and iodine molecules. This state would be highly unstable and the complex can break into two HI or H_2 and I_2 molecules depending on a chance happening. Such a complex is called an *activated complex*. If we plot the potential energy as a function of progress of reaction (defined by the extent of approach of the reactant molecules), the curve described in Fig. 5.8 is obtained.

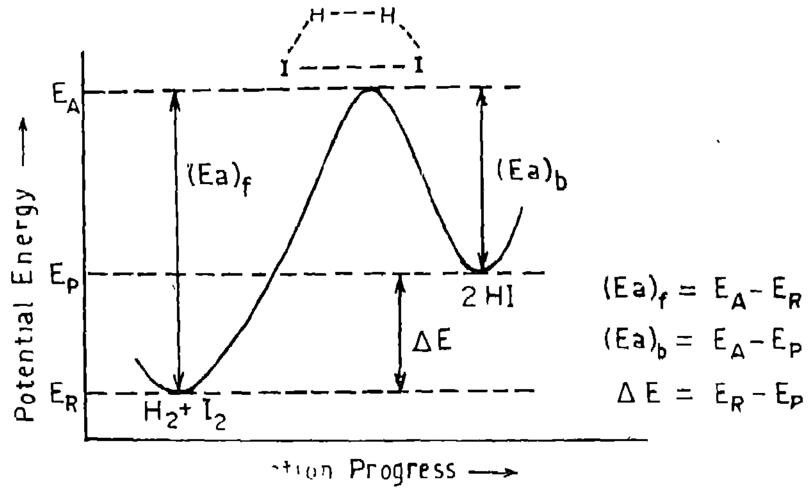


Fig. 5.8 Potential energy diagram for H_2 and I_2 reaction system (an endothermic reaction).

Initially, the reactants, H_2 and I_2, are in a stable situation when far apart and the potential energy of the system, E_R, is minimum*. When H_2 and I_2 molecules start approaching each other, the system becomes unstable and potential energy starts increasing. The potential energy attains a maximum value, E_A, when the activated complex is formed. Again, the potential energy decreases when the complex breaks into two molecules of HI. The potential energy goes on decreasing till the two molecules are sufficiently separated and another minimum value, E_P is obtained for the product molecules. From Fig. 5.8, it is apparent that, for the production of HI from H_2 and I_2, the potential energy of the reactants has to be first enchanced from E_R to E_A. The difference $E_A—E_R$ is called the *energy barrier* for the forward reaction and is equal to activation energy $(E_a)_f$ for the forward reaction. Similarly, the activation energy for the back reaction would be equal to E_A-E_P or $(E_a)_b$. The diagram also gives an idea about the sign of the energy change, E_P-E_R during the reaction. In the present case, energy is absorbed in the forward reaction, and this reaction is endothermic. In case of an exothermic reaction, potential energy diagram would be as shown in Fig 5.9. Here E_A for the activated complex is again the largest energy factor, but E_P is less than E_R, such that E_P-E_R or $\triangle E$ for the reaction is a negative quantity.

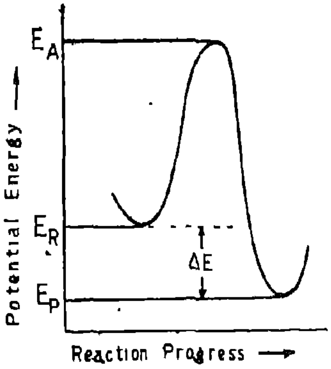


Fig 5.9 Potential energy diagram for exothermic reaction.

Thus, we find that energy of activation for any reaction is the difference between the potential energy of the activated complex and the potential energy of the reactants. Unless the colliding molecules have energy greater than this, the energy barrier cannot be crossed and the product molecules cannot be obtained. As pointed out earlier, the fraction of molecules having energy greater than the energy of activation is quite small and hence all collisions are not effective. Reactions involving free and reactive atoms have low or zero values for energy of activation and, in such cases, all or most molecular collisions become effective collisions.

5 12 INFLUENCE OF RADIATION ON CHEMICAL REACTIONS

It was pointed out in Section 5.1 that although the dark reaction between H_2 and Cl_2 is extremely slow, it becomes explosive when the reaction mixture is exposed to sunlight. Chlorine molecules absorb energy from light waves and, hence, become activated enough to decompose into chlorine atoms which are very reactive. Subsequently, a chlorine atom reacting with hydrogen molecules produces one molecule of HCl and a hydrogen atom. The hydrogen atom in turn reacts with a chlorine molecule producing another HCl molecule and a chlorine atom, and in this way a reaction chain is set up and the reaction rate becomes very fast.

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*It is known from a study of mechanics that potential energy is minimum in the stable state.

The sequence of steps can be represented as follows

$$Cl_2 \xrightarrow{\text{Light}} 2Cl^\bullet$$
$$Cl^\bullet + H_2 \longrightarrow HCl + H^\bullet$$
$$H^\bullet + Cl_2 \longrightarrow HCl + Cl^\bullet$$
$$M + H^\bullet + H^\bullet \longrightarrow M + H_2$$
$$M + Cl^\bullet + Cl^\bullet \longrightarrow M + Cl_2$$

The last two reactions are responsible for the termination of the chain reaction w M is the third (inert) body on which the recombination of atoms takes place.*

5 13 INFLUENCE OF A CATALYST ON RATE OF REACTION

A *catalyst* is a substance which increases the rate of a reaction without being used up in the end It can be recovered practically completely when the reaction is over. Presence of a catalyst in a reaction does not change its stoichiometry. If a reaction is not permitted by thermodynamic considerations, it cannot be helped by a catalyst. Catalysts help only the spontaneously possible chemical reactions It is not the mere presence of a catalyst that enhances the rate of the reaction. A catalyst actually participates in the reaction scheme. It is consumed in one step and regenerated in another subsequent step. A catalyst operates by providing an alternative mechanism for the reaction This mechanism involves a step or steps with lesser activation energies than the uncatalyzed reaction (Fig. 5.10) Thus, for the same total number of molecular collisions, a much larger fraction proves as effective collisions in case of catalyzed reaction.

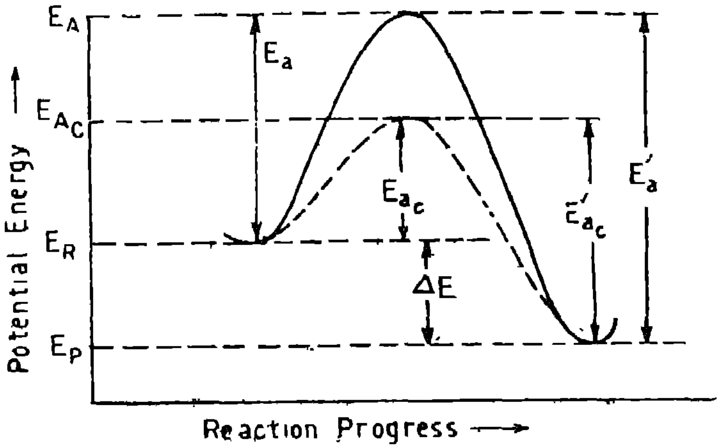

Fig. 5·10 Potential energy diagram for catalyzed and uncatalyzed mechanism for a reaction (Dotted line curve shows catalyzed reaction whereas solid line curve shows uncatalyzed reaction.)

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*Chemistry Textbook, Part I, p. 241.

Fig. 5.10 shows that (i) the reaction is an exothermic one, (ii) activation energy without the catalyst, E_a, is more than the activation energy $(E_a)_c$ when the catalyst is present, (iii) the energy change, $\triangle E$, is the same for the catalyzed and uncatalyzed reactions, and (iv) energy of activation of the forward and the reverse reactions are decreased by the same amount when the catalyst is present. A catalyst enhances the forward and the reverse reaction rates to the same proportion.

Table 5 4 shows that the energies of activation are considerably reduced in catalyzed reactions

TABLE 5.4

Activation Energies of Some Catalyzed Reactions

Reaction	Catalyst	Energy of activation (kJ/mol)
$2NH_3 \rightleftharpoons N_2+3H_2$	None	326
	W	163
	Mo	134-176
	Fe	159-176
	Os	197
$2SO_2+O_2 \rightleftharpoons 2SO_3$	None	251
	Pt	63

A catalyst influences the value of the rate constant k for a reaction. The rate constant acquires a much larger value when a catalyst is in use.

There are two important types amongst catalyzed reactions. If a catalyst is in the same phase as the reactants, the catalysis is said to be *homogeneous*. If the catalyst is in a different phase than the reactants, the catalysis is then said to be *heterogeneous* In most of the latter type of cases, the catalyst is a solid or a powder, while the reactants constitute a gaseous or a liquid solution. Adsorption plays a very important role in the working of heterogeneous catalysts. We shall read more about adsorption in Unit 8 of this book

Homogeneous catalytic reactions The combination of SO_2 and O_2 in the gaseous media is catalyzed by nitric oxide gas in the lead chamber process for the manufacture of SO_3.

$$SO_2+O_2 \xrightarrow{NO} SO_3$$

Hydrolysis of esters, e.g. methyl acetate, proceeds by itself very slowly, but it is greatly accelerated in the presence of hydrogen ions (supplied by a strong acid, e.g HCl) or hydroxyl ions (from NaOH).

$$CH_3COOCH_3+H_2O \xrightarrow[{[OH^-]}]{[H^+]} CH_3COOH+CH_3OH$$

Heterogeneous catalytic reactions · The rates of many chemical reactions are greatly increased by solid catalysts. Some industrial reactions, carried out by the use of heterogeneous catalysts, are as given below.

(i) In the manufacture of hydrogen from water gas by the Bosch process, ferric oxide with a promoter is used as a catalyst

$$CO + H_2O \xrightarrow[673\text{-}723K]{Fe_2O_3} CO_2 + H_2$$

Another method for the preparation of hydrogen is the reaction between methane and steam, using nickel catalyst at 1023-1173K

$$CH_4 + H_2O \xrightarrow{Ni} CO + 3H_2$$

This is used where natural gas is available

(ii) The preparation of methanol from CO and H_2 is carried out using zinc oxide as catalyst and Cr_2O_3 as a promoter

$$CO + 2H_2 \xrightarrow{ZnO} CH_3OH$$

(iii) Vegetable oils are hydrogenated in presence of finely divided nickel catalyst to obtain margarine.

$$\underset{\text{unsaturated oil}}{X\text{-}CH = CH\text{-}Y} + H_2 \longrightarrow \underset{\text{saturated fat}}{X\text{-}CH_2\text{-}CH_2\text{-}Y}$$

(iv) Hydrogen chloride is manufactured by passing the mixture of hydrogen and chlorine over activated charcoal.

(v) Cracking of petroleum is done under the influence of heat and suitable catalyst (e.g. a mixture of alumina and silica). By this means heavy oils can be made to yield petrol for cars and aeroplanes.

5.14 REVERSIBLE REACTIONS

Many reactions can proceed in the forward as well as in the reverse directions under the same experimental conditions (Sec. 7.2, Unit 7, Part 1). Such reactions are called *reversible reactions* and are indicated by using the $\rightleftharpoons$ sign in place of the usual single arrow sign. The reaction $H_2 + I_2 \rightleftharpoons 2HI$ is a typical example of a reversible reaction Another one is the reaction, $N_2O_4 \rightleftharpoons 2NO_2$

Let us consider a simple reversible reaction, which is unimolecular from both sides

$$A \underset{k_r}{\overset{k_f}{\rightleftharpoons}} B$$

Let us suppose that the rate constant for the forward reaction is k_f, while for the reverse reaction, the rate constant is k_r. Thus,

$$\text{Rate of the forward reaction} = k_f[A] \qquad \ldots(5.22)$$

$$\text{Rate of the reverse reaction} = k_r(B) \qquad \ldots(5.23)$$

Assuming that these reactions obey the first order reaction kinetics, at equilibrium we shall have :

Rate of forward reaction = rate of reverse reaction, so that :

$$k_f[A]_{eq} = k_r[B]_{eq}$$

$$\text{Hence, } \frac{[B]_{eq}}{[A]_{eq}} = \frac{k_f}{k_r} = K$$

where the subscript *eq* denotes equilibrium quantities and K is the equilibrium constant Thus, K is the ratio of rate constants for the forward and reverse reactions.

5 15 ENZYME CATALYSIS

Physiological reactions are much more complicated than the ones we have considered so far. Amongst this class we have enzymatic reactions. Enzymes act as catalysts for very specific reactions It is supposed that first of all an enzyme forms a complex with the molecule of a reactant called *substrate*. Denoting the enzyme by E and the substrate by S, the reaction can be written as

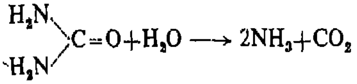
$$\underset{\text{enzyme}}{E} + \underset{\text{substrate}}{S} \rightleftharpoons \underset{\text{complex}}{ES}$$

Subsequently, the complex ES breaks into the product as follows .

$$\underset{\text{complex}}{ES} \longrightarrow \underset{\text{enzyme}}{E} + \underset{\text{product}}{P}$$

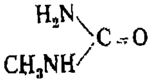
Thus, in an enzymatic reaction we have a reversible reaction step followed by a reaction step proceeding in one direction only.

An enzyme acts as a catalyst only for a particular substrate. For example, urease catalyzes the hydrolysis of urea



$$(H_2N)_2C{=}O + H_2O \longrightarrow 2NH_3 + CO_2$$

but it is ineffective in the hydrolysis of substituted ureas such as methyl urea having the formula .



$$(H_2N)(CH_3NH)C{=}O$$

In fact, there is a lock-and-key type relationship for enzyme action This is illustrated by Fig. 5.11. Enzymes help in carrying out reaction at body temperature which otherwise would need much higher, temperatures

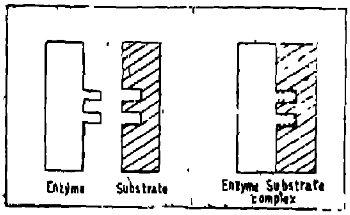


Fig 5.11 Formation of an enzyme-substrate complex

Two examples of enzyme catalyzed reactions are .

(i) $\text{starch} \xrightarrow{\text{diastase}} \text{maltose} \xrightarrow{\text{maltase}} \text{glucose} \xrightarrow{\text{zymase}} \text{alcohol} + CO_2$

(ii) $\text{cane sugar} \xrightarrow[+H_2O]{\text{invertase}} \text{invert sugar} \xrightarrow{\text{zymase}} \text{alcohol} + CO_2$

Diastase is present in malt and maltase, zymase and invertase are present in yeast.

EXERCISES

5.1 What are the factors which affect the rate of a chemical reaction ? Explain why rise in temperature increases the rate of reaction. Also explain (at the molecular level) why an increase in concentration of a reactant may cause an increase in the rate of reaction

5.2 Two gases X and Y are filled in a container, what effect will the following changes have on the rate of the reaction between these gases ?
  (i) The pressure is doubled
  (ii) The number of molecules of gas X is doubled
  (iii) The temperature is decreased at constant volume

5.3 Explain the following terms .
  (i) Activation energy
  (ii) Heterogeneous catalysis
  (iii) Homogeneous catalysis
  (iv) Reversible reaction

5.4 What is the difference between
  (i) Order of reaction and molecularity
  (ii) Enzymes and ordinary catalyst
  (iii) Heterogeneous and homogeneous reaction

5.5 Suggest explanations for :
  (i) The increased speed of a simple bimolecular change when the temperature of the reaction mixture is increased.
  (ii) The action of a solid phase catalyst to increase the rate of unimolecular gas-phase decomposition reaction
  (iii) One gram of pulverized wood burns faster than one gram piece of wood

5.6 An increase in temperature of 10 K rarely doubles the kinetic energy of the particles and hence the number of collisions is not doubled Yet, this temperature increase may be enough to double the rate of a slow reaction. How can this be explained ?

5.7 In a collision of particle, what is the primary factor that determines whether a reaction will occur ?

5.8 Discuss the following .
  (i) Activated complex
  (ii) Collision theory of reaction kinetics
  (iii) Endothermic and exothermic reactions
  (iv) Effect of catalyst on the activation energy
  (v) Rate constant

5.9 Sketch a potential energy diagram which might represent an endothermic reaction (label parts of curve representing activated complex, activation energy, net energy absorbed).

5.10 Find the two-third-life, $t_{\frac{2}{3}}$ of a first order reaction in which $k=5.48 \times 10^{-14}$ sec^{-1}

5.11 A first order reaction is found to have a rate constant $k=7.39 \times 10^{-5}$ sec^{-1}. Find the half-life of the reaction.

5.12 Identify the reaction order from each of the following rate constants .
  (i) $k=5.7 \times 10^{-5}$ sec^{-1}
  (ii) $k=9.3 \times 10^{-4}$ mole litre^{-1} sec^{-1}
  (iii) $k=6.2 \times 10^{-2}$ litre mol^{-1} sec^{-1}
  (iv) $k=2.8 \times 10^{-5}$ litre mol^{-1} sec^{-1}

(Hint. For 380 order, rate of reaction $\frac{dx}{dt}=k$)

5.13 What are enzymes ? How do they affect the rate of a chemical change ?

5.14 For a certain reaction it takes 5 minutes for the initial concentration of 0.5 mol litre^{-1} to become 0.25 mol litre^{-1} and another 5 minutes to become 0.125 mol litre^{-1}. What is the rate constant of the reaction ?

5.15 First order rate constants for the decomposition of dinitrogen pentoxide at various temperatures are as follows :

T (K)	273	298	305	318	328	338
k (sec^{-1})	7.9×10^{-7}	3.5×10^{-5}	1.35×10^{-4}	5.0×10^{-4}	1.5×10^{-3}	4.9×10^{-3}

Draw a graph and from it determine the activation energy for the reaction

UNIT 6

Solutions

When we place a lump of sugar or sodium chloride in water, it starts disappearing and becomes a part of the liquid Here, molecules or ions of the solute, through a bombardment of solvent molecules on the solid surface, leave the surface of the solid and, because of their acquired kinetic energy and continuous collisions with solvent molecules, they are dispersed throughout the entire bulk, resulting into a homogeneous mixture. Similarly, when ethyl alcohol is added to water, a clear homogeneous liquid mixture is obtained. In this case also the mixing of the two liquids occurs at molecular level. Each of the above types of homogeneous mixture of two or more substances having uniform properties (such as density, refractive index, etc) throughout is called a *solution*

The substances making up a solution are called *components* of the solution. In a binary solution, i.e. a solution made of two components, the component having the same physical state as the solution, is termed as the *solvent*, and the other component, the *solute*. In a situation in which none of the components has the same physical state as the solution or both have the same state as the solution, it is convenient to call the component present in excess, the solvent and the minor component, the solute Whereas each component of a solution has a fixed density, melting point or vapour pressure, such properties of their solutions vary according to composition. In this Unit, we shall study in some detail the properties of solutions, specially liquid solutions

6.1 TYPES OF SOLUTIONS

Solutions may exist in the gaseous, liquid or solid states. Prior to making a solution, the components thereof may be in the same or different states than that of the final solution. For a binary solution, depending on the physical state of the components, the following phase pairs are possible for solution components .

gas-gas
solid-gas
gas-liquid
liquid-liquid
liquid-solid
solid-solid

However, according to physical state of the solution after mixing its components, solutions can be solid, liquid or gaseous in form.

Gaseous Solutions : Since all gases and vapours form homogeneous mixtures, all gas mixtures are solutions. Such solutions are formed spontaneously and quickly. because of translatory motion of molecules in gases. Air is an example of gaseous solutions.

Liquid Solutions · These may be obtained as a mixture of two substances which are themselves liquids (g. water and ethyl alcohol) or may result from addition of a solid or a gas to a liquid. Some solid substances can form liquid solutions on mixing. A mixture of sodium and potassium metals in equimolar quantities is liquid at room temperature.

Unlike gases, all liquids do not form solutions on mixing. Liquid pairs can be *miscible* (completely soluble in each other in all proportions, e.g. mixtures of ethyl alcohol and water), *partially miscible* (such as mixtures of ether and water which show a limited solubility in each other), and *immiscible* (such as mixtures of oils and water). The question before us is why some liquids are miscible and others are not? A study of such systems shows that the liquids which are chemically alike dissolve in one another more freely than others. Alkanes, for instance, are so alike that their molecules naturally intermingle and they are, consequently, miscible in all proportions. But alkanes do not dissolve in water. The reason for this is simple. Water molecules are firmly held together by hydrogen bonds and alkane molecules are incapable of weakening those bonds. Similarly, the hydrogen bonds prevent the water molecules from mixing with alkanes. Ethanol has a property of dissolving both in organic solvents (such as the alkanes) and in water Here, the ethyl group of ethanol is similar to alkane molecules. The hydrogen bonding between hydroxyl groups of ethanol molecules, although weaker than that in water, is strong enough to allow ethanol molecules to push apart water molecules and thus ethanol dissolves in water with the formation of new hydrogen bond between water and ethanol molecules. Water molecules play the same role amongst ethanol molecules

Dipole-dipole interactions also play an important part in the formation of liquid solutions. Another factor to consider is molecular sizes. Molecules of liquid which dissolve in each other are often of approximately same size.

The general rule, *like dissolves like*, is also extendable to solutions of solids in liquids Inorganic substances which are polar in nature dissolve much more in polar solvents such as water or liquid ammonia than the nonpolar ones like alkanes or benzene.

Compositions of liquid solutions are usually expressed in terms of concentrations (Different ways of expressing concentration are given in the next section)

Since liquid solutions are of great importance to the chemists, we shall have a more detailed discussion of such solutions and more particularly of dilute solutions which present relatively less difficulties.

Solid Solutions : Although solid solutions are not so common as liquid solutions, they are nevertheless important. Such solutions are common in case of mixtures of metals. Gold and copper form a solid solution (since gold atoms can replace copper atoms in the copper crystal and, similarly, copper atoms can replace gold atoms in the gold crystal). Many alloys are solid solutions of two or more metals, e.g. constantan (60% Cu, 40% Ni). Many metals take up gases in large quantities to form solutions of gases in metals. For example, palladium is capable of taking up to 0.25 mole of molecular hydrogen per mole of metal at room temperature to form a solid solution of hydrogen in the metal. Non-electrolytes can also form solid solutions. Chlorobenzene and bromobenzene mix in all proportions in solid state. In forming solid solutions, chemical similarity and nearness of molecular sizes play a very important role.

6.2 METHODS FOR EXPRESSING CONCENTRATIONS OF SOLUTIONS

The concentrations of solutions can be expressed in a number of ways. A few of them are given below. For simplicity, we shall consider a solution made of two components A and B.

Mass Fraction. This is expressed as mass of a component per unit mass of solution.

Mass fraction (W_A) of component A can be expressed as $W_A = \frac{w_A}{w_A + w_B}$, where w_A is the mass of component A and w_B the mass of component B in a unit mass of solutions.

Mass percentage of component A will be equal to $W_A \times 100$

Mole Fractions : This is the number of moles of a particular component per unit total mole of solution. Accordingly, mole fraction of component A, χ_A, will be expressed as :

$$\chi_A = \frac{n_A}{n_A + n_B}$$

where n_A and n_B are the numbers of moles of A and B respectively in a fixed quantity of the solution. For example, a solution containing 23 g of ethanol and 90 g of water contains $\frac{23}{46}$ or 0.5 moles of ethanol and $\frac{90}{18}$ or 5 moles of water. Therefore, mole fraction of ethanol will be $\frac{0.5}{0.5 + 5.0}$ or 0.091.

Molarity (M) : It is expressed as the number of moles of a solute per litre of a solution. Suppose, component B is the solute. Then, molarity of the solution is expressed as $M = \frac{n_B \text{ moles}}{V \text{ litre}}$. Here, V is volume of solution in litres. Molarity is a convenient measure of concentration and is widely used in laboratory practice. One of its disadvantages is that the molarity of a solution changes with temperature because of expansion or contraction of the liquid.

While mass fractions and mole fractions are expressible in positive numbers, molarities are expressed in units of moles per dm^3. The symbol M used for molarities includes the units. Thus, a 0.5M solution of a substance represents a solution in which 0.5 mole of the solute is present in one litre of solution.

Molality (m) : This is expressed as the number of moles of solute (component B) per 1000g. (1kg) of solvent (component A). If n_B is the number of moles of solute and w_A is the number of grams of solvent, the molality of solution m_B, is given by

$$m_B = \frac{1000}{w_A} n_B$$

The molality of a solution does not change when the temperature of solution increases or decreases

Parts per Million (ppm) This is usually used for the mixtures or solutions where a substance is present in a very small quantity. The concentration of A in parts per million, ppm_A, is defined as

$$ppm_A = \frac{\text{mass of } A}{\text{total mass}} \times 10^6$$

6 3 VAPOUR PRESSURES OF SOLUTIONS AND RAOULT'S LAW

We have seen that if a pure liquid is covered with a bell jar, a part of the liquid evaporates and fills the available space with the vapour. At a particular temperature, an equilibrium is established between the vapour and liquid phases Pressure exerted by the vapour in such a situation at a given temperature is called the *vapour pressure* of the liquid (Unit 5, Part I). Now, if a nonvolatile solute is added to a solvent to make a solution, the vapour pressure of the solution will in fact be the vapour pressure of the solvent in it This vapour pressure is found to be less than that of the pure solvent.

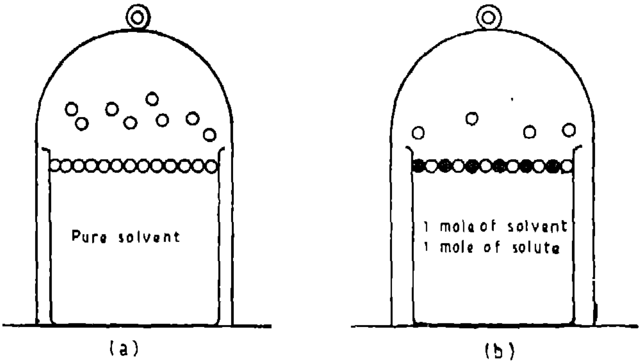


Fig 6.1 Decrease in the vapour pressure when a solute is added to a solvent (a) evaporation of molecules from the surface of pure solvent denoted by o, (b) in a solution solute particles denoted by ● also occupy a part of the surface area and so reduce the number of solvent molecules at the surface that evaporate (escape is reduced)

Evaporation of a liquid at any temperature below its boiling point is limited to the surface part of the liquid Thus, dependence of vapour pressure of solvent from a solution on the surface concentration of solution is quite expected, and its lesser value is easily explained. We may extend this consideration to the case when the solute is another volatile liquid or solid The vapour phase will then consist of vapours of components A and B of solution. We may well expect that partial vapour pressure of each component of the solution will depend on its molar concentration or mole fraction in solution.

Let us consider a solution of two miscible liquid components *A* and *B*. If mole fractions of *A* and *B* are χ_A and χ_B respectively, their partial vapour pressures P_A and P_B respectively above solution will be proportional to the respective mole fractions in the solution. Thus,

$$P_A \propto \chi_A$$

and $$P_B \propto \chi_B$$

Based on experimental vapour pressure data, Raoult showed that in case of mixtures of two miscible liquids, the above relation can be written as

$$P_A = P_A^\circ \chi_A \text{ and } P_B = P_B^\circ \chi_B \qquad (6.1)$$

P_A° and P_B° represent the vapour pressures of pure components *A* and *B*. The relationship between vapour pressure of a component and its mole fraction is referred to as *Raoult's law*, which states . *For a solution of volatile liquids, the partial vapour pressure of each component in the solution is directly proportional to its mole fraction.* (The law will not apply if a mixture of the volatile liquids does not form a solution.)

According to Raoult's law, a plot of P_A or P_B against χ_A or χ_B for a solution should give a straight line (straight lines I and II in Fig 6.2) passing through the points P_A° or P_B° when χ_A or χ_B equals unity. The total vapour pressure, *P*, exerted by the solution as a whole at any composition is given by the sum, $P_A + P_B$ (as required by Dalton's law of partial pressure). This is indicated in Fig 6.2 by the line III, joining the points P_A° and P_B°. The solutions for which Raoult's law is applicable are called *ideal solutions*. For such solutions, the vapour pressures are intermediate between the values, P_A° and P_B° and they all lie on the straight line joining P_A° and P_B° (Fig 6 2)

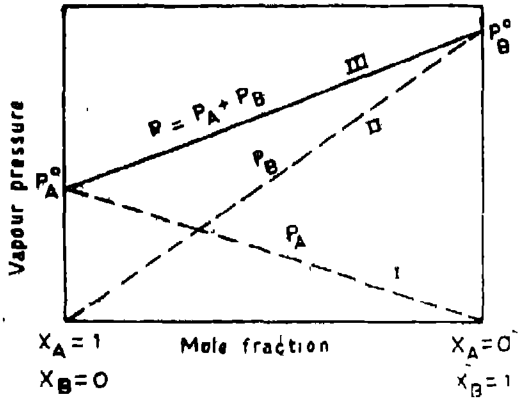


Fig. 6.2 The relationship at constant temperature between vapour pressure and mole fraction of an ideal solution. The dashed lines I and II represent the partial pressures of the components. (It can be seen from the plot that P_A and P_B are directly proportional to χ_A and χ_B, respectively.) The total vapour pressure is given by line III

Let us revert to a solution which is obtained by adding a nonvolatile solute to a volatile solvent (e.g. glucose and water) In such a case, there is no contribution from the solute and vapour pressure of solution will be only due to the solvent. The total vapour pressure here will be equal to vapour pressure contribution of the solvent in the solution. Therefore, if mole fraction of the solvent in a solution decreases, the vapour pressure of the solution will also decrease. Thus,

$$P = P_A = P^\circ_A . \chi_A \qquad \ldots\ldots\ldots(6.2)$$

Since, for a binary mixture, $\chi_A + \chi_B = 1$, $\chi_A = (1 - \chi_B)$ Therefore, we can write Eq. 6.2 in the form :

$$P_A = P^\circ_A(1 - \chi_B) \text{ or } \frac{P_A}{P^\circ_A} = 1 - \chi_B$$

By rearrangement, $1 - \frac{P_A}{P^\circ_A} = \chi_B$

Therefore, $\frac{P^\circ_A - P_A}{P^\circ_A} = \chi_B \qquad \ldots\ldots..(6.3)$

In Eq. 6.3, $(P^\circ_A - P_A)$ represents the lowering of vapour pressure on formation of solution and $(P^\circ_A - P_A/P^\circ_A)$ is called the relative lowering of vapour pressure for the solution Thus, an alternative statement of Raoult's law for solutions of non-volatile solutes can be given as : *Relative lowering of vapour pressure for a solution is equal to the mole fraction of the solute when solvent alone is volatile.* An understanding of Raoult's law and its extension to solution of nonvolatile solutes is essential to explain the behaviour of solutions.

6.4 IDEAL SOLUTIONS

As stated in Section 6.3, *ideal solutions are those which obey Raoult's law.* The properties of an ideal solution are, essentially, the average of the properties of its components in proportion to their mole fractions. Thus, an ideal solution consisting of an equal number of moles of *A* and *B* will have a vapour pressure exactly midway between the vapour pressures of *A* and *B*, as we have seen in the previous section.

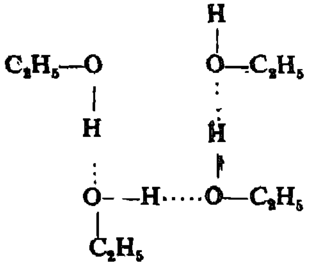
If two liquids *A* and *B* form an ideal solution, the *A-A* and *B-B* molecular interaction forces will be the same and there will be little or no net change in the molecular interaction forces on solution formation. This means that the force of attraction between *A* and *B* molecules (i.e. A-B molecular interaction forces) will be the same as those for the *A-A* or *B-B* molecules. Such a solution can form only when the substances composing them are identical in structure and polarity. Liquids, like hexane and heptane, when mixed together in any proportion form nearly ideal solutions, since in these solutions the hexane-hexane attractions, the heptane-heptane attractions and the hexane-heptane attractions are almost the same. Truly speaking, ideal solutions are quite rare but quite a number of them are practically ideal in behaviour. Other examples of solutions which are ideal for all the practical purposes, are mixtures of ethyl bromide and ethyl iodide, benzene and toluene, chlorobenzene and bromobenzene, etc. By progressive dilution, all solutions tend to reach a state of ideal behaviour.

As there is no change in interaction forces between two components when they are mixed to form an ideal solution, heat change on mixing, ΔH_{mixing} in such cases will be zero. Moreover, in such cases, the volume of the solution is the sum of the volumes of the components before mixing. Volume change on mixing, ΔV_{mixing} is also zero. Thus, the conditions for an ideal solution formation are :

(i) Raoults' law should be satisfied
(ii) $\triangle H_{mixing}$ should be zero
(iii) $\triangle V_{mixing}$ should be zero

6.5 NON-IDEAL SOLUTIONS

Most pairs of miscible liquids form non-ideal solutions. Sometimes, partial vapour pressure of a component is found to be more than what is allowed by Raoult's law on adding another component. A similar effect is observed for the other component in the reversed mixing. The total vapour pressure for any solution is thus greater than that corresponding to an ideal solution of the same composition The boiling points of such solutions are relatively lowered. Such behaviour of solutions is described as a *positive deviation* from Raoult's law (Fig 6.3) For one of the intermediate compositions, the total vapour pressure of such a solution will be the highest and the boiling point will be the lowest. This solution acquires the property of boiling at a constant temperature and remains unchanged in composition. Liquid mixtures which can distil unchanged in composition are called *azeotropes* or *azeotropic mixtures*. In case of positive deviations, we get *minimum boiling (point) azeotropes*. The positive deviations are exhibited by liquid pairs for which the *A-B* molecular interaction forces are lower than the *A-A* or the *B-B* molecular interaction forces. Mixtures of ethanol and cyclohexane behave in this way. In pure ethanol, a very high fraction of the molecules are hydrogen bonded. On adding cyclohexane, the cyclohexane molecules get in between the molecules of ethanol, thus breaking up the hydrogen bonds and markedly reducing the ethanol-ethanol intermolecular attractions. In case of positive deviations for a liquid pair we should expect a slight increase in volume and absorption of heat on mixing. Same are the actual observations.



Hydrogen Bonding in Ethanol

On the other hand, if for the two components *A* and *B*, the interaction forces between the *A* and *B* molecules are more than the *A-A* and *B-B* interaction forces, the escaping tendency of *A* and *B* types of molecules from the solution becomes less than from the pure liquids. In other words, for any solution composition, the partial vapour pressure of each component will be less and the total vapour pressure of the solution will also be less than that required by Raoult's law (Fig 6.4). These solutions are said to show *negative deviations* from Raoult's law. Such solutions exhibit an increase in boiling points on adding more of the solute. For one of the intermediate compositions, the total vapour pressure of the solution will be the least and the boiling point will be the highest. This solution will also distil without a change in composition and provides an example of another kind of azeotrope. We call it the *maximum boiling (point) azeotrope*. Negative deviation from Raoult's law is exhibited by mixture of chloroform and acetone. When chloroform (trichloromethane) $CHCl_3$, and acetone $(CH_3)_2CO$, are mixed, the hydrogen bonding occurs between the two molecular species. This decreases the escaping tendency of molecules for each component and, as a result, the boiling points of solutions show an increase. An evidence of hydrogen bonds being formed is provided by the fact that when these two components are mixed, the temperature rises (ΔH is negative). In case of negative deviation, we should also expect contraction in volume on mixing along with evolution of heat. A few examples of the mixtures which show positive and negative deviations from ideal behaviour are given in Table 6.1

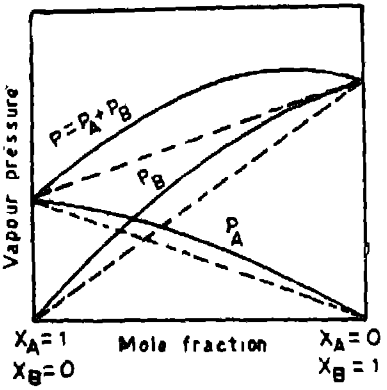


Fig. 6.3 A vapour pressure graph showing a positive deviation (solid lines) from ideal behaviour (dotted lines)

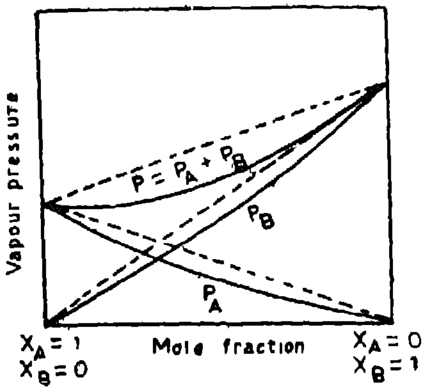
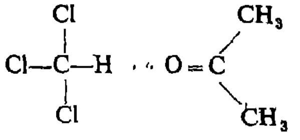


Fig. 6.4 A vapour pressure graph showing a negative deviation (solid lines) from ideal behaviour (dotted lines).



Hydrogen Bonding between Chloroform and Acetone

Apart from hydrogen bonding, there are other weaker intermolecular forces also which may be responsible in part for observed deviations from ideal behaviour. A more detailed account cannot be given in the present course.

TABLE 6.1
Non-Ideal Mixtures

Mixtures showing positive deviations	Mixtures showing negative deviations
$(CH_3)_2CO + CS_2$	$CH_3COOH + C_5H_5N$ (pyridine)
$(CH_3)_2CO + C_2H_5OH$	$CHCl_3 + (CH_3)_2CO$
$C_6H_6 + (CH_3)_2CO$	$CHCl_3 + C_6H_6$
$CCl_4 + C_6H_6$	$CHCl_3 + (C_2H_5)_2O$
$CCl_4 + CHCl_3$	$H_2O + HCl$
$CCl_4 + C_6H_5.CH_3$	$H_2O + HNO_3$
$H_2O + CH_3OH$	$(CH_3)_2CO + C_6H_5NH_2$
$H_2O + C_2H_5OH$	

6 6 COLLIGATIVE PROPERTIES,

We have learnt about vapour pressure-composition relationships of solutions in the previous sections. Whatever be the non-idealities shown by such solutions, they tend to behave more ideally when we proceed towards greater dilutions. There are some interesting properties of such dilute solutions which have important applicatio-- These properties do not depend on the nature of the solutes, but only on the molar concentrations in solutions It means that two solutions made from different components may show identical values of some properties dependent only on mole fractions in the solutions. Such dependence of a property of a dilute solution on the mole fraction of the solute can be expressed as follows .

Property measured $\propto$ *mole fraction of the solute*

Let us consider a system of two components A and B, where A is the solvent and B is the solute. Suppose masses of the solvent and solute are w_A and w_B and their molecular masses are M_A and M_B respectively. Moles of solvent, $n_A = \frac{w_A}{M_A}$, and moles of solute. $n_B = \frac{w_B}{M_B}$.

Therefore. mole fraction of solvent, $\chi_A = \frac{n_A}{n_A + n_B}$

Mole fraction of solute, $\chi_B = \frac{n_B}{n_A + n_B}$

Now, the properties measured being proportional to $\frac{n_B}{n_A + n_B}$,

$$\text{Colligative property} = \text{A constant} \times \frac{n_B}{n_A + n_B}$$

$$= \text{A constant} \cdot \frac{\frac{w_B}{M_B}}{\frac{w_A}{M_A} + \frac{w_B}{M_B}} \qquad \text{........(6.4)}$$

Eq. 6.4 may be used for calculating the value of any of the involved factors when the values of all the rest are known.

Properties of solution which depend only on the mole fraction of the solute in it (i e on the relative molar proportion of solute and solvent in a solution) are called *colligative properties*. These properties are widely used for the determination of molecular masses of substances. Here, we will consider the following colligative properties (i) Relative lowering of vapour pressure for a solution, (ii) Elevation of boiling point for a solution, (iii) Depression of freezing point for a solution, and (iv) Osmotic pressure for a solution

6 7 . RELATIVE LOWERING OF VAPOUR PRESSURE

We have seen in the previous section that relative lowering of vapour pressure of a solvent in a solution of nonvolatile solute is equal to the mole fraction of the solute. i.e

$$\frac{P_A^\circ - P_A}{P_A^\circ} = \chi_B$$

As lowering of vapour pressure depends on the mole fraction of the solute and not on its chemical nature, it constitutes a colligative property and can be used for determination of molecular masses. The above expression can be written as :

$$\frac{P_A^\circ - P_A}{P_A^\circ} = \chi_B = \frac{\frac{W_B}{M_B}}{\frac{W_A}{M_A} + \frac{W_B}{M_B}}$$

Thus, if lowering of vapour pressure is found for a solution of known concentration and molecular mass of *A* is known, the molecular mass of *B* can be worked out from the above expression. But it is difficult to measure the vapour pressure lowering accurately. Therefore, molecular mass determination by this method is often difficult. However, as a consequence of the lowering of vapour pressure of a solvent, significant changes occur in some other properties of solvents in solutions. These properties, notably the melting and boiling points, are relatively easier to measure.

6.8 ELEVATION OF BOILING POINTS

Lowering of vapour pressure of a liquid solvent on addition of a nonvolatile solute has some interesting consequences. We know that the normal boiling point of a liquid is the temperature at which its vapour pressure becomes equal to one atomospheric pressure. The normal boiling point of water is 373 K, since at this temperature vapour pressure of water is one atmosphere. Vapour pressure of a liquid is always lowered due to the addition of nonvolatile solute (Fig 6.5). Vapour pressure of an aqueous glucose solution at 373K is less than one atmosphere. This means that we need to heat the solution to a higher temperature than 373K for the vapour pressure value to reach one atmosphere. Hence, boiling point of any solvent in a solution with a nonvolatile solute is always higher than the boiling point of the pure solvent. Thus, such solutions show an elevation in boiling points and, at their boiling points, they are in equilibrium with pure solvent vapour.

Let ΔT_b be the elevation in boiling point and Δp the lowering of vapour pressure Then, ΔT_b is found to be proportional to Δp

$$\Delta T_b \propto \Delta p \propto \chi_B$$

$$\text{or } \Delta T_b = K.\ \chi_B \qquad (6.5)$$

Where K is a proportionality constant.

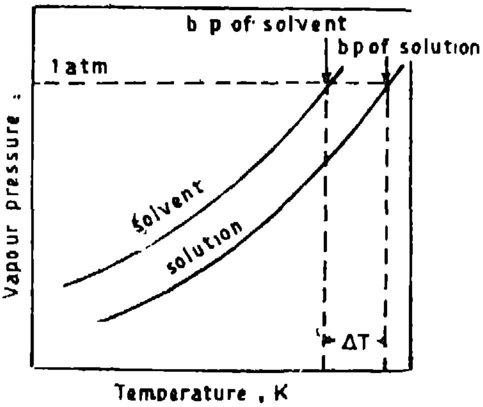


Fig 6.5 Elevation of boiling point of a solution.

As we have seen in Eq. 6.4,

$$\chi_B = \frac{\frac{w_B}{M_B}}{\frac{w_A}{M_A}+\frac{w_B}{M_B}}$$

If the solution is dilute and $\frac{w_B}{M_B} \ll \frac{w_A}{M_A}$ we may write :

$$\chi_B = \frac{\frac{w_B}{M_B}}{\frac{w_A}{M_A}} = \frac{M_A . w_B}{M_B . w_A} = n_B . \frac{M_A}{w_A} \qquad \text{.........(6.6)}$$

Molality of a solution is defined as the number of moles of the solute per kilogram of solvent. If in Eq. 6.6 we take the mass of the solvent, w_A, in kilogram units, n_B/w_A will stand for the molality, m, of the solution and we can modify Eq. 6.6 to Eq. 6.7.

$$\chi_B = M_A . m \qquad \text{........(6.7)}$$

Combining Eqs. 6.5 and 6.7, we have :

$$\Delta T_b = K M_A m = k_b m \qquad \text{........(6.8)}$$

The new proportionality constant (k_b) relating the elevation of boiling point for the solution with its molality is called the ***molal boiling point elevation constant*** for the solvent. Thus, molal boiling point elevation constant is numerically equal to the elevation in boiling point observed for 1 molal solution (prepared in a particular solvent) Molal elevation boiling point constants have characteristic values for different solvents. Some of such values are given in Table 6.2 k_b values are expressed as degrees/molality or as K/m* or °*C*/*m* For water, $k_b = 0.52°C/m$ or 0.52K/m This means that a 1 molal solution of any normal solute in water has a boiling point 0.52 degree higher than that of water itself under the same atmospheric pressure.

TABLE 6.2

Molal Boiling Point Elevation and Freezing Point Depression Constants for Some Solvents

Solvent	b.p (K)	k_b (K/m)	f.p. (K)	k_f (K/m)
Water (H_2O)	373.0	0.52	273.0	1.86
Ethyl alcohol (C_2H_5OH)	351.5	1.20	155.7	1.99
Benzene (C_6H_6)	353.3	2.53	278.6	5.12
Chloroform ($CHCl_3$)	334.4	3.63	209.6	4.70
Carbon tetrachloride (CCl_4)	350.0	5.03	250.5	31.8
Carbon disulphide (CS_2)	319.4	2.34	164.2	3.83
Ether ($C_4H_{10}O$)	307.8	2.02	156.9	1.79

6.9 DEPRESSION OF FREEZING POINTS

The lowering of vapour pressure of a solvent in a solution is also closely related to the depression of freezing point for the solution If, at the freezing point, a solution is in equilibrium with the pure solid form of the solvent, the freezing point of the solution will be lower than that of the pure solvent. This is shown in Fig. 6.6. The lowering observed at the freezing point, ΔT_f, is also found to be proportional to the mole fraction of the solute. As in the case of elevation of boiling points, we can now write .

$$\Delta T_f \propto \chi_B \qquad \text{.........(6.9)}$$

$$\text{or } \Delta T_f = K.\chi_B$$

$$\text{Since } \chi_B = \frac{\frac{w_B}{M_B}}{\frac{w_A}{M_A} + \frac{w_B}{M_B}}$$

$$\Delta T_f = K \cdot \frac{\frac{w_B}{M_B}}{\frac{w_A}{M_A} + \frac{w_B}{M_B}} \qquad (6.10)$$

Here, *K* is a proportionality constant. In case of dilute solutions for which ideal solution relationships are valid, w_B/M_B will be very much smaller than w_A/M_A and we can write (as in the case of elevation of boiling points) ;

---

*K/m represents kelvin/molality.

$$\Delta T_f = K.\frac{w_B.M_A}{w_A.M_B} = KM_A.\frac{w_B/M_B}{w_A}$$

$$= KM_A\frac{n_B}{w_A} = k_f m \quad .. (6\ 11)$$

When n_B is the number of moles of solute present for w_A kilograms of the solvent, k_f is called the *molal freezing point depression constant* or *molal cryoscopic constant* for the solvent It equals, numerically, the freezing point depression of molal ideal solution in the solvent. Thus, $k_f = \frac{\Delta T_f}{m} = K.M_A$. As for k_b, k_f values will also have the unit of degree/molality or K/m or °C/m.

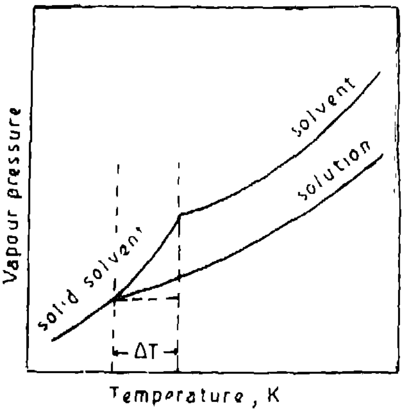


Fig 6 6 Depression of the freezing point of a solution

Experimentally, it has been found that one mole of a normal solute in 1000g or 1kg of water lowers the freezing point of water by 1.86° Thus, molal freezing point depression constant for water is 1.86 deg/molality Each solvent has a characteristic value of k_f Values of k_f for some solvents are given in Table 6 2.

6.10 OSMOTIC PRESSURE

We now come to the last of the colligative properties—osmotic pressure

In the middle of the eighteenth century it was observed that there are certain membranes which, when placed between a solution and the solvent present in it, allow passage across to the solvent molecules, but do not permit solute molecules or ions to pass through These membranes are said to be *semipermeable* Such membranes are frequently found in living systems, but the actual mechanism of how these membranes operate is not fully understood as the solute molecules which cannot pass through the membranes are sometimes smaller than the solvent molecules which do pass through

When a semipermeable membrane separates a solvent from a solution, solvent molecules tend to pass from the solvent side into the solution In case, two solutions of different concentrations are separated by a semipermeable membrane, the solvent molecules will pass from the dilute solution side onto the more concentrated solution side. This movement of solvent through a semipermeable membrane is called *osmosis* Osmosis can be demonstrated by a simple apparatus shown in Fig. 6 7

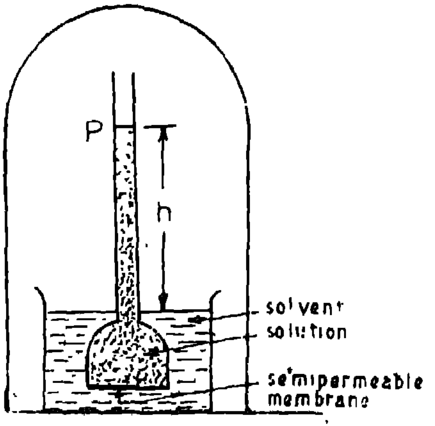


Fig 6.7 Osmosis and osmotic pressure : Osmotic pressure developed will be equal to hydrostatic pressure of the liquid of height h.

As shown in Fig 6.7, as the solvent enters into the funnel due to osmosis, the level of the solution in the tube rises. A stage comes when level in the tube becomes stationary at P Here, the hydrostatic pressure of the solution at the membrane due to the height of the liquid column becomes sufficiently high to push out as much solvent as is drawn in due to osmosis Thus, no further flow of solvent into the funnel is observed *The extra pressure to be applied on the solution side necessary to counteract the pressure due to osmosis when the solution and the solvent are separated by a semipermeable membrane is a measure of the osmotic pressure of solution.* It is possible to check osmosis from occurring by applying a mechanical pressure on the solution equal to its osmotic pressure

Let us consider the case in which we have the solution and solvent on two sides of a semipermeable membrane At a given temperature, the solution has a vapour pressure lower than that of the corresponding pure solvent. We can regard and calculate osmotic pressure as the extra pressure that must be exerted on a solution in order that the vapour pressure of solvent from the solution increases and becomes equal to that of pure solvent Only then will the solution be in an equilibrium with the pure solvent on the other side of the smipermeable membrane. The movement of solvent during osmosis can also be checked by applying a suction or negative pressure on the side of the solvent. Such suction pressure can also be equated with the osmotic pressure

Measurement of osmotic pressure is usually done with an apparatus shown in Fig 6.8 The solution is placed in a strong steel vessel which can stand the high counter pressures applied, to it. A semipermeable membrane imbedded in a porous pot separates the solution reservoir from the pure solvent central reservoir The semipermeable membrane is a wall of an inorganic material* that permits only the flow of solvent molecules to and fro but not of solute molecules

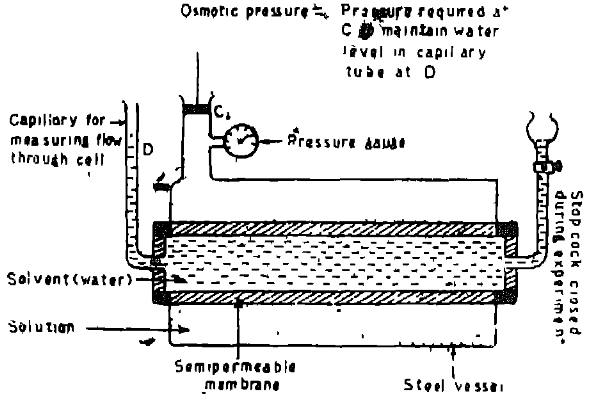

Osmotic pressure = Pressure required at C to maintain water level in capillary tube at D
C
Capillary for measuring flow through cell
D
Pressure gauge
Stop cock closed during experiment
Solvent (water)
Solution
Semipermeable membrane
Steel vessel

Fig 6.8 Osmostic pressure measurement (Berkeley and Hartley method)

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*A semipermeable membrane can be formed in the walls of a porous pot by allowing solution of copper sulphate and potassium ferrocyanide to meet inside the walls. A precipitate of potassium coppe ferrocyanide, deposited uniformly in the pores of the pot, acts as a good semipermeable membrane

Like the other colligative properties, such as depression of freezing point and elevation of boiling point, osmotic pressure is also related to the lowering of vapour pressure and is in turn proportional to the mole fraction of solute. We can write for the osmotic pressure, π,

$$\pi = K\chi_B \tag{6.12}$$

The constant K in this case is found to be equal to RT/V_A. Hence,

$$\pi = \chi_B \frac{RT}{V_A} \tag{6.13}$$

where V_A is volume of one mole of the solvent, A; χ_B is the mole fraction of solute B in the solution and R is a constant equal to the gas constant. If R is expressed in units of litre atm deg^{-1} mol^{-1}, T in kelvins and V_A in litres, osmotic pressure obtained will be in units of atmospheres. Since, $\chi_B = \frac{n_B}{n_A + n_B}$, the mole fraction χ_B can be approximated to $\frac{n_B}{n_A}$ in the case of dilute solutions (when $n_A \gg n_B$). The osmotic pressure relationship then becomes,

$$\pi = RT \frac{n_B}{n_A V_A} = \frac{n_B}{v} RT = cRT \tag{6.14}$$

If $v = n_A V_A$ = volume of n_A moles of solvent $\simeq$ total volume of the solution (since the volume contribution due to solute in a dilute solution can be considered as negligible) and c represents the molar concentration of solute in the solution, we can write Eq. 6.14 as,

$$\pi v = n_B . RT \tag{6.15}$$

Eqs 6.14 and 6.15 are the two forms of *van't Hoff osmotic pressure formula* or van't Hoff's solution equation.

The similarity between van't Hoff's equation, $\pi v = n_B RT$ and the perfect gas equation, $Pv = nRT$, and appearance of molar gas constant R in both equations reflects that gas pressures and osmotic pressures of solutions have some common relationship with kinetic energies of particles.

Using Eq. 6.15, osmotic pressure of any solution can be calculated. Osmotic pressure of a solution containing 0.1 mole of solute per litre at 273 K is calculated below.

$$\pi = \frac{n_B}{v} \cdot RT = \frac{0.1}{1} \times 0.08205 \times 273 = 2.224 \text{ atm}$$

Thus, we see that, even for quite dilute solutions, osmotic pressures are of the order of atmospheres. This makes accurate measurements of osmotic pressures quite convenient even for very dilute solutions.

6 MOLECULAR MASSES FROM COLLIGATIVE PROPERTIES

Molecular masses of volatile liquids and gases can be determined by applying Avogadro's law (Unit 19, Part I). But this method cannot be applied to nonvolatile substances such as urea and sugar. For such substances, measurement of colligative properties such as elevation of boiling point, depression of freezing point, and osmotic pressure of a solution provide convenient methods for determination of molecular masses. We have seen in this Unit that colligative properties depend on the number of moles of the dissolved substances. Therefore, if k_f or k_b be known for a solvent and if the concentration of the solution be known, molecular mass of the solute can be calculated using the appropriate relationships.

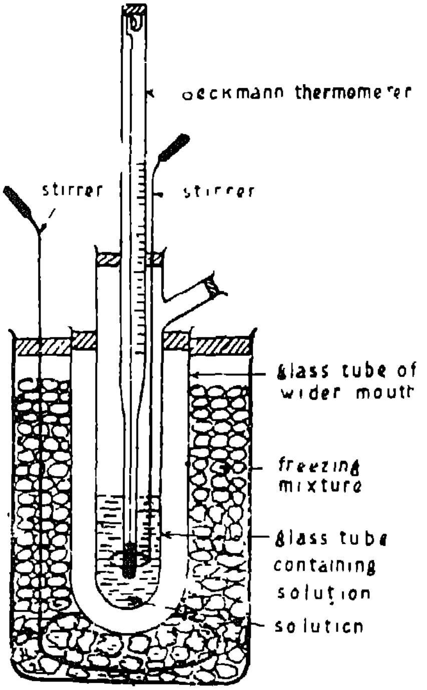


Fig. 6.9 An apparatus for determination of depression of freezing point

In practice, freezing point method is most commonly used because the change in freezing point for a solution is larger than the change in boiling point for it (compare constant K_f and k_b for water). A simple diagram of the apparatus used for the determination of molecular mass by depression of freezing point method is given in Fig. 6.9

The boiling point elevation method, however, gets the advantage of higher solubilities of solutes due to an increase in temperature. Osmotic pressure measurements are frequently used to determine the molecular masses of compounds like synthetic polymers and biologically important compounds like proteins. Because of low solubilities of such substances, molar concentration of solutions are ordinarily low in such cases and, thus, very dilute solutions are obtained. The following examples illustrate the calculation steps

Example 6.1

A solution of 1.25 g of a certain non-electrolyte in 20.0 g of water freezes at 271.94 K. Calculate the molecular mass of the solute ($k_f = 1.86$ K/m)

Solution

For depression in freezing point of a solution,

$$\Delta T_f = k_f\, m$$

Molality, *m*, of a solution is given by moles of solute present per kg or 1000g of solvent. In terms of w_A, w_B and M_B in grams, molality is given by .

$$m = \frac{w_B/M_B}{w_A} \times 1000$$

$$\text{Hence.}\ \Delta T_f = k_f\, \frac{w_B.1000}{M_B.w_A}.$$

and $M_B = k_f \frac{w_B.1000}{w_A \Delta T_f}$

$w_A = 20.0g$

$w_B = 1.25g$

$\Delta T_f = 273 - 271.94$

$= 1.06K$

$K_f = 1.86K/m$

Substituting the data provided, we get,

$$M_B = \frac{1.86 \times 1.25 \times 1000}{20 \times 1.06} = 109.6 \text{ g/mol}$$

Example 6.2

Osmotic pressure of a solution containing 7g of dissolved protein per 100 cm³ of solution is 25 mm Hg at body temperature (310K). Calculate the molecular mass of the protein (R = 0.08205 lit atm mol⁻¹ deg⁻¹)

Solution

We know, $\pi v = n_B RT$

In the present problem,

$$\pi = \frac{25}{760} \text{ atm, } v = 100\text{cm}^3 = 0.1 \text{ litre, } T = 310\text{K,}$$

$$n_B = \frac{7}{M_n} \text{ mol and } R = 0.08205 \text{ lit atm mol}^{-1} \text{ deg}^{-1}$$

Therefore, we get :

$$\frac{25}{760} \times 0.1 = \frac{7}{M_B} \times 0.08205 \times 310$$

or $M_B = 5.4 \times 10^4$, or 54,000 g/mol

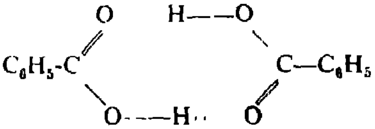
Thus, molecular mass of the protein will be 54,000 g/mol

6.12 ABNORMAL MOLECULAR MASSES

We have seen in the previous section that colligative properties are used for the determination of molecular masses. It has also been stated that the relationships used for the determination of molecular masses are valid only for ideal behaviour of solutions. It has been observed that the value of molecular mass determined by using lowering of vapour pressure, depession of freezing point, elevation of boiling point, and osmotic pressure data do not always agree with the normal values. This may be due to : (i) deviation of solutions from ideal behaviour, (ii) association of solute molecules, or (iii) dissociation of the solute molecules.

Deviations of solutions from ideal behaviour have already been discussed. Here, we shall consider the other two possibilities.

In general, when there is association, the solute consists of a mixture of single molecules, double molecules, and possibly their larger associations. Therefore, the measured experimental value of molecular mass may be greater than the normal one for completely unassociated molecules Association of solute molecules in a solution is generally caused by hydrogen bonding between these molecules. This is observed in the case of compounds capable of forming hydrogen bonds, e.g. alcohols, phenols, carboxylic acids. When acetic acid, CH_3COOH, and benzoic acid, C_6H_5COOH, are dissolved in benzene it is found that the solute particles have molecular masses of nearly 120 and 244 respectively, which are just twice their normal values To account for this observation, it has been suggested that molecules must exist in solution as dimers, held together by hydorgen bonds.



(Solvents which prevent association of the solute are those that can themselves take part in hydrogen bonding, e.g water and alcohol).

In certain cases, where bonding is not so strong as it is for carboxylic acids and association is not limited to only formation of dimers, the value of molecular mass increases with concentration and varies from a little more to several times the normal value

It has been found that molecular masses obtained from solutions of strong electrolytes (e g. strong acids, strong bases and salts) are much less than their normal values. This is because these electrolytes are dissociated into ions, e.g. $KCl(s)+H_2O(l) \rightarrow K^+(aq)+Cl^-(aq)$ Here, each KCl unit is broken into two particles (ions). Therefore, molecular mass in the solution should be mean of the masses of the two ions K^+ and Cl^- which is equal to exactly half the molecular mass of KCl. However, depression of freezing point method gave a molecular mass equal to 40.3 which is greater than the theoretical value $\frac{(39.1+35.5)}{2}$. This difference between the two figures is due to strong attractive forces existing between oppositively charged ions in a solution. These attractive forces are much stronger than the normal intermolecular attraction. First, they cause deviations from Raoult's law which is the basis for molecular mass determination and, secondly, the electrical forces may permanently hold a fraction of the ions together as *ion pairs*: each ion pair consisting of one positive and one negative ion. It has been found that majority of the ionic substances appear to be incompletely dissociated because of ion pairing, but a small number of salts (including alkali halides) are dissociated into separate ions When an electrolytic solution is diluted, the average distance between ions increases and, therefore, coulombic attractive forces decrease and become less important. In very dilute solution, the observed molecular masses tend towards the complete dissociation values

In 1886, van't Hoff introduced a factor i, known as van't Hoff's constant to express the extent of association or dissociation. The factor i can be written as .

$$i = \frac{\text{Normal molecular mass}}{\text{Observed molecular mass}}$$

In case of association, values of i will be less than unity. In case of dissociation, however, they will be greater than unity. For very dilute solution of KCl, i would be 2. However, if the solutions are stronger, i will be less than 2.

EXERCISES

6.1 What is the effect of temperature upon vapour pressure ? Describe in terms of kinetic theory what happens when a system of liquid and vapour in equilibrium is (i) heated, and (ii) cooled down.

6.2 Calculate the mole fraction of alcohol, C_2H_5OH and water in a solution made by dissolving 9.2 g of alcohol in 18.0 g of water

6.3 0.212 g of sodium carbonate, Na_2CO_3, molecular mass 106g/mol, is dissolved in 250 cm^3 of solution. Calculate the molarity of Na_2CO_3 in the solution.

6.4 A solution is 25% water, 25% ethanol and 50% acetic acid by mass. Calculate the mole fraction of each component.

6.5 Determine the molality of a solution formed by dissolving 0.850 g of NH_3 in 100 g of water.

6.6 Explain the following terms :

(i) Mole fraction, (ii) Molarity, (iii) Molality, (iv) Ideal solution, (v) Colligative property

6.7 A solution of sucrose (mol. mass, 342 g/mol) is prepared by dissolving 68.4g in 1000g of water What is

(i) the vapour pressure of the solution at 293K ?
(ii) the osmotic pressure at 293K ?
(iii) the boiling point of the solution ?
(iv) the freezing point of the solution ?

The vapour pressure of the water at 293K is 17.5 mmHg. Take any of the information required from the text, and assume the solution to behave ideally.

6.8 When two miscible liquids (A and B) are mixed there is often a temperature change accompanying the establishment of the A$\longleftrightarrow$B molecular interaction. Recalling that thermal energy is released when structure is created, what temperature changes would you predict for the mixing of the two liquids whose solution showed a negative deviation from Raoult's law ?

6.9 Carbon tetrachloride and water are immiscible whereas ethyl alcohol and water are miscible in all proportions. Correlate this behaviour with the molecular structures of the three compounds

6.10 Benzene, C_6H_6(b.p. 353.1K) and toluene, C_7H_8(b.p. 383.6K) are two hydrocarbons that form a very nearly ideal solution. At 313K the vapour pressure of pure liquids are benzene, 160 mmHg, toluene, 60 mmHg. Assuming an ideal solution behaviour, calculate the partial pressures of benzene and toluene, and the total pressure over the following solutions

(i) one made by combining equal numbers of toluene and benzene molecules
(ii) one made by combining 4 moles of toluene with 1 mole of benzene
(iii) one made by combining equal masses of toluene and benzene.

6.11 Find the (i) boiling point, and (ii) freezing point of a solution containing 0.520g glucose ($C_6H_{12}O_6$) dissolved in 80.2 g of water. For water k_f=1.86 K/m.

6.12 What is Raoult's law ? Discuss the factors responsible for deviation from this law by taking suitable examples.

6.13 An aqueous solution of a weak monobasic acid containing 0.1g in 21.7g of water freezes at 272.813K. If the value of k_f for water is 1.86 K/m, what is the molecular mass of the monobasic acid?

6.14 A solution of 12.5g of urea in 170g of water gave a boiling point elevation of 0.63 K. Calculate the molecular mass of urea taking $k_b = 0.52$ K/m. Derive any formula used.

6.15 What is osmotic pressure ? How will you determine the molecular mass of a substance with this method ? What are the conditions for getting accurate value of molecular mass of a substance

6.16 At 298K, 100 cm^3 of a solution, containing 3.002 g of an unidentified solute, exhibits an osmotic pressure of 2.55 atmospheres. What would be the molecular mass of the solute ?

6.17 When fruits and vegetables that have dried are placed in water, they slowly swell and return to original form. Why ? Would a temperature-increase accelerate the process ? Explain.

6.18 The normal freezing point of nitrobenzene, $C_6H_5NO_2$ is 278.82K. A 0.25 molal solution of a certain solute in nitrobenzene causes a freezing point depression of 2 degree Calculate the value of k_f for nitrobenzene.

6.19 Why do you get sometimes abnormal molecular masses of the substances by using colligative properties of the solution ? State the factors with suitable examples which bring abnormality in the result thus obtained.

UNIT 7

More About Electrochemistry

Unit 8 of Part I is dealt with a study of *electrolysis* and other related aspects of it. Electrolysis is a set of electrochemical reactions occurring at the surface of electrodes when an electric current is passed through an electrolyte. Here, chemical changes are brought about at the cost of electrical energy. In the present Unit we shall be dealing with generation of electrical energy through chemical changes.

7.1 ELECTROCHEMICAL CHANGES

These are chemical changes in which electric currents flow over finite distances larger than molecular sizes. They are of two kinds (i) those in which electrical energy is absorbed (*electrolysis*), and (ii) those which produce electric currents as a result of electron transfer chemical reactions.

In an electron transfer reaction, the substance losing electrons is said to be *oxidized* and the one gaining electrons is *reduced*. Since in any electron transfer reaction a gain and a loss of electrons occur simultaneously, such coupled reactions are called *redox* changes. A redox change is considered as a chemical reaction, if the electron transfer occurs directly between two substances over a distance of separation of the order of one or a few molecular diameters. Thus, if we place a plate of zinc metal in a solution of copper sulphate, immediately the following reaction occurs

$$Zn(s)+Cu^{2+}(aq)\rightarrow Zn^{2+}(aq)+Cu(s)$$

In this change, zinc atoms lose electrons to copper ions. Since the two are in direct contact, the electron transfer is direct and across a separation no larger than a molecular diameter. Thus, this redox change is a chemical reaction. It is, however, possible to carry out a transfer of electrons from zinc metal to copper ions indirectly when the two are separated in different vessels by making an arrangement as shown in Fig 7.1. In this arrangement, the zinc metal loses electrons to copper ions through the connecting wire and the copper plate dipped in a copper sulphate solution. The oxidation and reduction processes are separated from each other.

Oxidation	$Zn(s)\rightarrow Zn^{2+}(aq)+2e$
Reduction	$Cu^{2+}(aq)+2e^{-}\rightarrow Cu(s)$
Redox change	$Zn(s)+Cu^{2+}(aq)\rightarrow Zn^{2+}(aq)+Cu(s)$

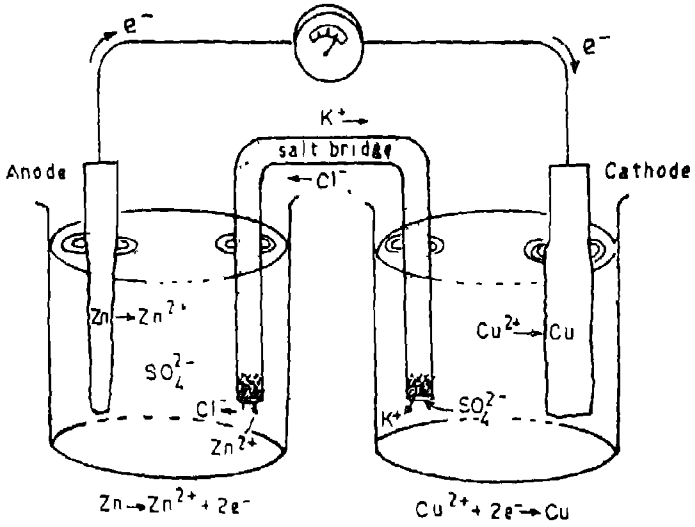


Fig 7.1 An arrangement showing an electrochemical change. (Electrons flow through the external circuit resulting into current, internal circuit is completed due to flow of ions through the salt bridge)

The redox change occurring under these conditions is an electrochemical change. Electrolysis cases are also redox changes of electrochemical type.

7.1-1 SALT BRIDGE AND ITS ROLE

Flow of an electric current requires unbroken contacts all over the circuit For providing contacts between solution of electrolytes, solutions of *inert electrolytes* can be used. Inert electrolytes are those whose ions are not involved in the electrochemical changes nor do they react chemically with the electrolytes electrically connected by them. The link electrolyte solutions are usually of salts and, hence, the name *salt bridge* for them. Salt solutions used for bridging are taken at higher concentrations than the electrolyte solutions linked by them. The most often used salt bridges are KCl and KNO_3 NH_4NO_3 is also used sometimes. The bridge is made with an agar gel. This arrangement prevents mechanical flow of solutions through the bridge, but provides free path for electrical migration of ions to maintain an electrical current through the involved electrolytes

Let us consider Fig. 7.1 without its salt bridge The electrons released by zinc atoms can flow up to the copper plate through external circuit. There they will neutralize some of the Cu^{2+} ions from the solution. When this has happened, for a short while the copper sulphate solution will acquire a negative charge due to loss of positive ions (Cu^{2+}ions). In the meantime, zinc sulphate solution will become positively charged with the new Zn^{2+} ions gained by it from the zinc plate Accumulation of charges in the two solutions will prevent further flow of electrons and the electrochemical changes will stop. When a salt bridge is used, it provides a passage for flow of charge in the internal circuit The negative ions move from the copper-plate end through copper sulphate solution, salt bridge and zinc sulphate solution to the zinc plate. The positive ions move in the reverse direction, i.e., from the zinc-plate side to the copper plate. Thus, a flow of electricity is maintained and an accumulation of charges is prevented when the salt bridge is used

7.2 SOME ELECTRICAL UNITS

It would be relevant to describe some of the electrical units which are very often used in the electrical measurements.

Coulomb : The coulomb is the amount of electricity required to deposit by electrolysis 0.001118g of silver from a solution having silver ions. In terms of electronic charges, 96,500 coulombs correspond to Avogadro's number (6.02×10^{23}) of electron charges. This larger unit of electricity is called a *faraday* Therefore,

1 faraday = 96,500 coulombs = 6.02×10^{23} electron charges

Ampere : The time rate of flow of electrons is measured in amperes One ampere stands for flow of one coulomb per second through an entire conductor.

A current of one ampere will take 96,500 seconds for flow of one faraday through a conductor. Therefore,

coulombs = amperes × seconds.

Ohm : It is a unit of resistance or opposition to the flow of electricity through a conductor. Ohm is the electrical resistance at 273K of a uniform thread of mercury 106.3 cm long and weighing 14.4521g.

Siemen . Electrical conductance of any conductor is the reciprocal of its resistance. Siemen is the unit of electrical conductance and is the reciprocal of ohm. It has been earlier called by various names like reciprocal ohm, mho and ohm inverse.

Volt : It is a unit of electrical potential (electrical pressure). A volt is the potential needed to send a current of one ampere through a resistance of one ohm. If one faraday (96,500 coulombs) of electricity is to be pushed through a resistance of one ohm in one second, a potential of 96,500 volts will be needed.

Watt : The unit of electrical energy is the same as for other forms of energy. It is the joule. A joule is the energy corresponding to flow of one coulomb of charge at a potential of 1 volt. Therefore,

joules = coulombs × volts

The time rate of supply of electrical energy (i.e. *electric power*) is measured in watts. One watt is the electrical power when one joule of electrical energy is made available in one second. Therefore,

$$\text{watts} = \frac{\text{joules}}{\text{seconds}} = \frac{\text{coulombs} \times \text{volts}}{\text{seconds}} = \text{amperes} \times \text{volt}$$

and, joule = watt × second

Watt-second **· It is a rather small unit of electrical energy. The commercial uni of electrical energy equals one *kilowatt-hour*.**

$$
\begin{aligned}
1 \text{ kilowatt-hour} &= 1000 \text{ watts} \times 3600 \text{ seconds}\\
&= 3.6 \times 10^6 \text{ watt-seconds}\\
&= 3.6 \times 10^6 \text{ joules} = 3.6 \times 10^3 \text{ kilo-Joules}\\
&= 3.6 \times 10^3 \text{ kJ}
\end{aligned}
$$

An electrical heater rated at 1000 watts consumes energy at the rate of 1000 joules per second or one kilowatt-hour (one commercial unit of electrical energy) in one hour

7.3 GALVANIC OR VOLTAIC CELLS

A cell like the combination shown in Fig 7.1, which can be used to supply electrical energy at the cost of chemical changes, is called a voltaic or a galvanic cell after Alessandro Volta (1800) or Luigi Galvani (1780) who first carried out experiments for conversion of chemical energy to electrical energy. Operation of a galvanic cell consists of coupled oxidation and reduction electrochemical changes taking place at two different electrodes The electrons released by the oxidation reaction are pushed out into the external circuit In Fig 7.1 oxidation occurs at the zinc electrode. This electrode is called the *anode* because of the oxidation taking place on it It is assigned *negative polarity* as it is electron rich and pushes out electron into the external circuit. In Fig 7.1, reduction is shown to occur at the copper electrode and because of it this electrode is called the *cathode* Since there is a demand of electrons at the copper electrode for affecting reduction of copper ions, therefore, the copper electrode becomes electron deficient and pulls in electrons from the external circuit. Due to its attraction for electrons, the reduction electrode is assigned a *positive polarity*. Thus. *anode for oxidation* and *cathode for reduction* is the rule for naming electrodes in electrochemical cells

One way of preventing mechanical mixing of two electrolyte solutions surrounding the anode and the cathode is to connect them with a salt bridge A less efficient but more practical method is to use a porous pot to separate these solutions. An example of this is the commercial form of Daniell cell (Fig 7.2).

A galvanic cell can be set up by coupling together any oxidation reaction with any reduction reaction provided suitable electrode metals and electrolyte solutions are available and they can be so arranged that chemical changes will not occur until the external circuit is completed by adding one or more metallic conductors

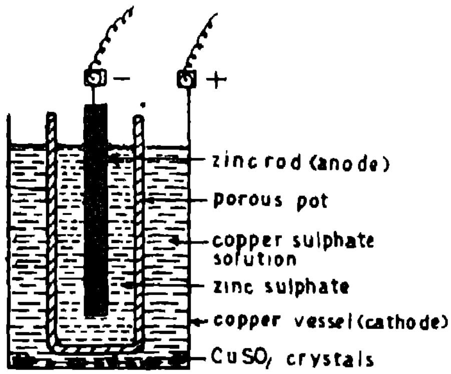


Fig. 7.2 Daniell cell (a simple galvanic cell).

7.3.1 SYMBOLIC REPRESENTATION OF GALVANIC CELLS

We have seen that a galvanic cell consists of two electrodes—anode and cathode.

These two electrodes are also referred as two *half cells* Thus, when two half cells are combined we get a cell. According to a universally accepted convention, when we represent a galvanic cell, anode is written on the left hand side This anode of the cell, i.e., half cell written in the left is represented by writing metal or solid phase first and then the electrolyte. The two are separated by a semicolon or a vertical line The electrolyte may be shown as ionic species or by the formula for the whole compound As additional information, concentrations may be also mentioned in bracket A few examples of representing anode of the cell are given below .

Zn,Zn^{2+} or Zn | Zn^{2+} or Zn; $ZnSO_4$ (0.1M)

Pt H_2(1atm),H^+(1 M)

Pt, H_2 (1 atm) stands for hydrogen and platinum together as a solid phase in which hydrogen is adsorbed under 1 atm pressure condition. Comma is used between Pt and H_2 to indicate that they form one phase

The cathode of a cell (at which reduction occurs) is written on the right hand side This is represented by writing the electrolyte first and the metal or solid phase thereafter, the two being separated by a semicolon or a vertical line. Some examples are cited below.

Cu^{2+}(1M); Cu or Cu^{2+} (1 m) | Cu

Cl^-(0.1M), Cl_2(1 atm), Pt

A half cell which functions as an anode in one galvanic cell may function as cathode in another galvanic cell depending upon combination.

For representing a galvanic cell, the anode and cathode formulations are combined In some galvanic cells, one and the same electrolyte solution can provide ions required for the two electrode reactions Then, no separation need be shown between the electrolytes of the two electrodes when combining the electrode formulations. An example of this type is the cell,

Pt. H_2(1 atm) H Cl (0.1M); Cl_2, Pt

in which HCl as an electrolyte provides H^+ ions for the hydrogen electrode and Cl^- ions for the chlorine electrode In other cases, where electrolytes used either differ in their species or in concentrations, and are in direct contact through a porous separation, are separated by a single vertical line (*not a semicolon*) Thus, Daniell cell using a porous pot can be shown as .

Zn,$ZnSO_4$, H_2SO_4 | $CuSO_4$ (satd.); Cu

and when a salt bridge is used it is indicated with two vertical lines separating the two half cells.

Zn;Zn^{2+}(1M) || Cu^{2+}(1M);Cu

7.4 ELECTRODE POTENTIALS

The difference of potentials between electrodes of a galvanic cell can be measured by using a voltmeter. This potential difference* is called the *electromotive force* (abbreviated to emf or EMF) of the cell if no, or very little, current is allowed to flow at the time of measurement of the potential difference The potential measuring device also fixes the positive and negative poles of the cell. Each electrode makes a contribution to the cell potential which we call the *electrode potential.* The measurement of single electrode potentials is not possible because during measurement whenever we dip a second metal into an electrolyte solution, it becomes an electrode itself and we get a new galvanic cell This difficulty in measuring single electrode potentials can be met by choosing one of the electrodes as a reference electrode and assigning to it a potential of Zero Volt The *normal hydrogen electrode* (NHE) has been universally accepted as a reference electrode at all temperatures and, even though its own potential at different temperatures is different, it has been assigned the zero volt value. For normal **hydrogen electrode, pure hydrogen kept at 1 atm pressure should bubble around a platinized platinum plate dipped into an acid solution with a hydrogen ion concentration of one mole per litre (1 *M* or 1 *N* solution). Potentials of all other electrodes can be found by coupling them with NHE. The EMF of a galvanic cell is measured and its value is assigned to the potential of the electrode.**

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*In normal cases potential differences are measured by potentiometer and potential difference thus obtained is emf at zero current

In case of every electrode, where the electrolyte is 1 molar in concentration, the solid phase consists of the pure substance or substances and if a gas is involved and it is at a partial pressure of one atmosphere, the electrode is called a *standard electrode* and its measured potential is called the *standard electrode potential* Cell and electrode potentials are given the symbol *E* and if standard electrodes are used, the EMF is given the symbol E°

The solid phase and the electrolyte for an electrode remain together in an equilibrium state. Thus, the equilibrium between Zn and Zn^{2+} in a solution can be represented as:

$$Zn(s) \rightleftharpoons Zn^{2+}(aq) + 2e^-$$

The forward reaction is the oxidation reaction and the reverse one the reduction reaction. Thus, all electrode systems are redox systems. When coupled with NHE, some electrodes undergo reduction reaction permitting NHE to undergo oxidation reaction. Other behaves in a reverse way when they undergo oxidation and reduction occurs at NHE. Every electrode can be made to undergo an oxidation or a reduction reaction by choosing an appropriate coupling electrode In fact, an electrode may accept electrons from the external circuit or push electrons into it, depending on the conditions under which it is operating. If, on combination with NHE, an electrode spontaneously undergoes reduction process, it is said to have a positive value of reduction electrode potential. It can also be said to have an equal but negative value of oxidation electrode potential. The negative sign of oxidation potential is to remind that the oxidation at the electrode (when coupled with NHE) will not be spontaneous. It can be only forced by using appropriate external potential. By the same argument, for an electrode which spontaneously undergoes oxidation change when coupled with NHE, it will have a positive value of oxidation electrode potential and a negative value of reduction electrode potential A simple scheme for determining standard electrode potential using NHE as a *standard* is shown in Fig 7.3

Next, we may think of drawing lists of standard electrode potentials for the known electrode systems. This can be drawn as standard oxidation electrode potentials or as standard reduction electode potentials. Since some (and not all) electrodes

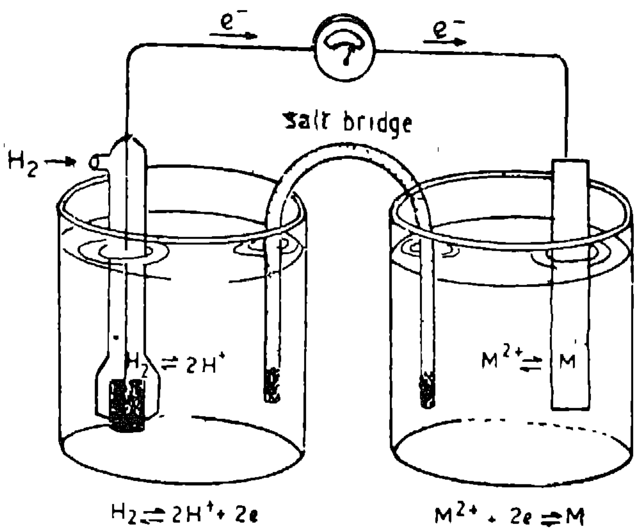

Fig 7 3 A scheme for determining the standard electrode potential (Hydrogen electrode is shown in the left)

undergo spontaneous reduction change when coupled with NHE, either of the lists will have some values positive and the others negative The list preferred these days is of standard reduction electrode potentials A partial list of common standard reduction electrode potentials is given in Table 7 1 One advantage of using the list of reduction

TABLE 7 1

Standard Reduction Electrode Potentials at 298K in Water*

Electrode	Electrode reaction (reduction)	E° (volts)
Li; Li^+	$Li^+ + e^- \longrightarrow Li$	−3.05
K, K^+	$K^+ + e^- \longrightarrow K$	−2.93
Ba, Ba^{2+}	$Ba^{2+} + 2e^- \longrightarrow Ba$	−2.90
Ca, Ca^{2+}	$Ca^{2+} + 2e^- \longrightarrow Ca$	−2.87
Na, Na^+	$Na^+ + e^- \longrightarrow Na$	−2.71
Mg; Mg^{2+}	$Mg^{2+} + 2e^- \rightarrow Mg$	−2.37
Al, Al^{3+}	$Al^{3+} + 3e^- \longrightarrow Al$	1.66
Zn; Zn^{2+}	$Zn^{2+} + 2e^- \longrightarrow Zn$	−0.76
Fe; Fe^{2+}	$Fe^{2+} + 2e^- \longrightarrow Fe$	−0.44
Pb, $PbSO_4$;SO_4^{2}	$PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}$	−0.31
Co, Co^{2+}	$Co^{2+} + 2e^- \longrightarrow Co$	−0.28
Ni; Ni^{2+}	$Ni^{2+} + 2e^- \longrightarrow Ni$	−0.25
Sn; Sn^{2+}	$Sn^{2+} + 2e^- \longrightarrow Sn$	−0.14
Pb; Pb^{2+}	$Pb^{2+} + 2e^- \longrightarrow Pb$	−0.13
Pt, H_2, H^+	$2H^+ + 2e^- \longrightarrow H_2$	+0.00
Cu; Cu^{2+}	$Cu^{2+} + 2e^- \longrightarrow Cu$	+0.34
Ag; Ag^+	$Ag^+ + e^- \longrightarrow Ag$	+0.80
Cl^-; Cl_2, Pt	$Cl_2 + 2e^- \longrightarrow 2Cl^-$	+1.36
Au; Au^{3+}	$Au^{3+} + 3e^- \longrightarrow Au$	+1.50
F^-; F_2, Pt	$F_2 + 2e^- \longrightarrow 2F^-$	+2.87

*Standard oxidation electrode potentials will have the same values with the sign reversed potentials is that the sign of the reduction potential is also the polarity sign of the electrode when coupled with NHE to construct a galvanic cell. *The more negative the reduction electrode potential for an electrode, the more powerful it will be in a competition for pushing out electrons into the external circuit.* Therefore, the more powerful it will be for undergoing the oxidation reaction and the more difficult it will be to reduce the corresponding ions in the electrolyte. Thus, metals like Li and K will readily provide electrons for reducing cations like Cu^{2+} and Ag^+.

7.4.1 ELECTRO-CHEMICAL SERIES

Half-cell potential or electrode potential indicate the relative ease with which the various involved species of metals and ions may be reduced or oxidized Thus, the high negative reduction electrode potential of the lithium electrode indicates that it will be very difficult to reduce Li^+ ions to Li atoms but it will be most easy for Li to get oxidized to Li^+ ions. It also indicates that it will be more difficult to reduce Li^+ ion than H^+ ion. So, when Li metal is added to a solution having H^+ ions, Li is oxidized to Li^+ and H^+ ions are reduced to H_2 gas. Further, if Li^+ ions are themselves very difficult to get reduced, they cannot easily accept electrons from other substances and will, therefore, be very poor oxidizing agent.

In Table 7 1, the most active metals occur at the top. We can, thus, make the general statement that the more negative the reduction electrode potential for a metal-metal ions electrode, the more reactive this metal will be in displacing other metals from their salts Thus the EMF series of Table 7.1 also provides the *activity series* or *electrochemical series* of metals. It is possible to demonstrate in the laboratory that any metal given in Table 7.1 displaces the metals given below it from their salt solution For example, copper lies just above silver, if copper foils are added in silver nitrate solution, silver is replaced from the solution. We can take many such examples

Half-cell potentials can be combined to get the galvanic cell potentials

7.5 ELECTRODE POTENTIALS AND ELECTROLYTE CONCENTRATIONS

We have considered the electrode potential of the electrode in the standard state In general, galvanic cells are operated under concentration conditions different from the standard-state conditions. The relationship between electrode potentials and concentrations of the involved substances in the electrode or half-cell reaction is given by Nernst equation For reduction electrode potentials, the half-cell reaction should be written as the reduction reaction. The concentrations of pure solids and liquids are regarded as unity The general reduction electrode reaction is ·

$$A^{n+} + ne^- \longrightarrow A$$

Nernst equation for the above reaction may be written as

$$E = E^\circ - \frac{2.30\ RT}{nF} \log \frac{[A]}{[A^{n+}]}$$

Using the values : $R = 8.314\ JK^{-1}\ mol^{-1}$, $T = 298K$ (usual value, the temperature at which E values are tabulated), and F = 96, 500 coulombs ·

$$E = E^\circ - \frac{0.059}{n} \log\frac{[A]}{[A^{n+}]}$$

Example 7.1

Calculate the half-cell potential at 298K for the reaction,

$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$, if $[Cu^{2+}]$ is $5.0M$ and E° is $+0.34$ volt.

Solution

According to Nernst equation

$$E = E^\circ - \frac{0.059}{2} \log\frac{[Cu]}{[Cu^{2+}]}$$

$$= 0.34 - \frac{0.059}{2} \log\frac{1}{5.0} = 0.34 - 0.0295(-0.70)$$

$$= (0.34 + 0.02) \text{ volt} = 0.36 \text{ V}$$

7.6 CELL POTENTIALS FROM ELECTRODE POTENTIALS

The EMF of a galvanic cell, E_{cell} can be readily calculated from the ***reduction half-cell potentials*** using the following relationship. For a cell formulation showing the anode on the left hand side and the cathode on the right hand side, the cell potential is given by

$$E_{cell} = E_{right} - E_{left} = E_{cathode} - E_{anode}$$

It should be remembered that in this relationship both half-cell potentials are reduction electrode potentials. A negative value of standard reduction potential of an electrode means that at this electrode reduction will not occur and oxidation will occur when this electrode is coupled with NHE. Similarly, if on calculating the cell potential according to above relationship we get a negative value, it will mean that in actual operation of the cell the electrodes will have reversed functions for what have been assigned to them.

Example 7.2

Claculate the standard cell potentials for the cells :

(i) Zn; $Zn^{2+}(1M)$ || $Cu^{2+}(1M)$;Cu

(ii) Ag; $Ag^{+}(1M)$ || $Cu^{2+}(1M)$; Cu

Solution

$$E_{cell} = E_{right} - E_{left}$$

(i) $E_{cell} = +0.34 - (-0.76) = 0.34 + 0.76 = 1.10$ V.

(ii) $E_{cell} = +0.34 - 0.80 = -0.46$ V

Here electrode potential values are taken from Table 7.1.

The positive value of E_{cell} for the first cell means that zinc will be the anode and copper will be the cathode of the cell. The negative value of E_{cell} in the second case means that in this cell Ag electrode will not be the anode; it will instead be the cathode and the anode function will take place on the copper electrode.

7.7 SOME ENERGY PRODUCING CELLS

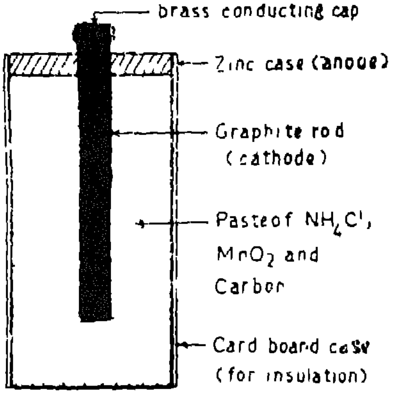
brass conducting cap
Zinc case (anode)
Graphite rod (cathode)
Paste of NH_4Cl, MnO_2 and Carbon
Card board case (for insulation)

Fig 7.4 A schematic representation of a dry cell

Daniell cell shown in Fig 7.2 is used in the laboratory as a source of electrical potentials. *Dry cells* used in batteries are based on the Lechlanche' cell. The latter uses a solution of ammonium chloride while the former uses a paste which does not flow. Fig 7.4 shows a dry cell construction. The central carbon or graphite cathode has a brass cap for better contact. This is the positive electrode of the cell. It is surrounded by a cloth bag containing a paste of NH_4Cl, MnO_2 and carbon powder. The zinc anode surrounds the paste and the cell has an outer insulation of a cardboard case. During use the zinc case gets consumed and in the end it will develop holes which are responsible for leakages. The so called leak proof dry cells have an iron or steel sheet covering the zinc. This is inert for the paste used. Thus, even when the zinc case is consumed, holes are not developed and no leakages occur. Actual reactions of the cell are complex. The reaction may be shown as:

Anode reaction : $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

Cathode reaction $2NH_4^+(aq) + 2MnO_2(s) + 2e^- \rightarrow Mn_2O_3(s) + 2NH_3(aq) + H_2O(l)$

Ordinary dry cells are not rechargable. We have on the market *rechargable dry cells* based on nickel-cadmium batteries. The electrode reactions are :

Anode reaction : $Cd(s) + 2OH^-(aq) \rightarrow Cd(OH)_2(s) + 2e^-$

Cathode reaction $NiO_2(s) + 2H_2O(l) + 2e^- \rightarrow Ni(OH)_2(s) + 2OH^-(aq)$

In this cell, no gas is formed or lost. The reaction products stick to the electrodes and can be reconverted by recharging the cell as for the lead storage battery used in motor cars.

EXERCISES

7.1 A conventional method of representing Daniell cell is
$Zn(s); Zn^{2+}(aq)(1M) \parallel Cu^{2+}(aq)(1M); Cu(s)$
(i) Draw a diagram of the cell and mark anode and cathode as current is drawn
(ii) Give the net reaction as current is drawn.
(iii) What is the cell potential at 298K ?

7.2 A cell is set up between copper and silver $Cu(s); Cu^{2+}(aq) \parallel Ag^+(aq); Ag(s)$
If the two half cells work under standard conditions, calculate the e m f of the cell

7.3 What are the standard electrode potentials for cells in which the following reactions occur :
(i) $Cu^{2+}(aq) + H_2(g) \rightarrow 2H^+(aq) + Cu(s)$;
(ii) $Cu^{2+}(aq) + Zn(s) \rightarrow Cu(s) + Zn^{2+}(aq)$
(iii) $2Cr(s) + 3Cu^{2+}(aq) \rightarrow 2Cr^{3+}(aq) + 3Cu(s)$?

7.4 Describe the following .
(i) Oxidation potential
(ii) Reduction potential
(iii) Normal hydrogen electrode

7.5 Explain the difference between .

(i) emf and potential difference

(ii) Electrochemical cell and electrolytic cell

(iii) Electron movement and ion movement

7.6 For each of the following standard cells, with the help of Electrode Potential Table, calculate E° and indicate that which electrode is anode.

(i) Al/ Al^{3+}(aq) versus Cu/ Cu^{2+} (aq)

(ii) Al/ Al^{3+}(aq) versus Mg/ Mg^{2+}(aq)

(iii) Cu/ Cu^{2+} (aq) versus Mg/ Mg^{2+}(aq)

7.7 In a simple electrochemical cell, which is in the standard state, the half-cell reactions with their appropriate oxidation potentials are :

$Pb(s) - 2e^- \rightarrow Pb^{2+}(aq)$, ($E^\circ = +0.13V$)

$Ag(s) - e^- \rightarrow Ag^+(aq)$, ($E^\circ = -0.80$ V).

Which of the following reactions take place ? Also calculate the EMF of the cell in the given condition,

(i) $Pb^{2+}(aq) + 2\ Ag(s) \rightarrow Ag^+(aq) + Pb(s)$

(ii) $Pb^{2+}(aq) + Ag(s) \rightarrow Ag^+\ (aq) + Pb(s)$

(iii) $Ag^+(aq) + Pb(s) \rightarrow Ag\ (s) + Pb^{2+}\ (aq)$

(iv) $2Ag^+(aq) + Pb(s) \rightarrow 2Ag\ (s) + Pb^{2+}\ (aq)$

7.8 Arrange the metals in an increasing order of the reactivity. Which one is the strongest reducing agent and which one will be the weakest ones :

Mg, Na, Ag, Cu, Fe, Zn

7.9 What are the uses of electrochemical changes ?

7.10 Write short notes on the following ·

(i) Salt bridge

(ii) Electrochemical series

(iii) Daniell cell

UNIT 8

Surface Chemistry

In this Unit we shall be concerned with situations in which surface properties of substances assume importance. Surface effects are predominant for rough surfaces and finely divided materials. Under these conditions, an appreciable part of a substance is present at or near surface The important phenomena to be considered under these conditions are *adsorption, colloidal state of substances* and *heterogeneous chemical reactions*

8 1 ADSORPTION

A surface separates two phases or material areas If at this surface some substance *A* has a concentration in the surface layer which is different from the concentration of *A* in the bulk phases, *A* is said to be *adsorbed* at the surface. The existence of a substance at a surface in a different concentration than in the adjoining bulk phases is called *adsorption* It differs from *absorption* in one important aspect. Absorption of a substance *A* by a substance *B* means that *A* is uniformly distributed all over *B* Adsorption, on the other hand, means that *A* may be present on the surface of *B* in a high concentration, but concentration of *A* in parts of *B* away from the surface will be nil or very low. This will be clear from Fig 8 1. The adsorbing bulk substance is called the *adsorbent* and the substance being adsorbed is called *adsorbate* The process of removing an adsorbed substance from a surface on which it is adsorbed is called *desorption*

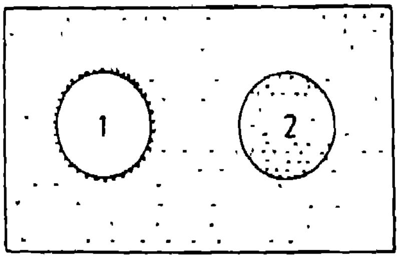

Fig 8 1 Simple representation of adsorption and absorption (Solid 1 has adsorbed the gas on its surface The interior has no gas Solid 2 has absorbed the gas uniformly)

Only surface particles on an adsorbent play an active role in adsorption These particles possess unbalanced or unutilized forces of various types such as van der Waals forces and even chemical bond forces. These come into existence as soon as a solid piece is broken into two to develop two new surfaces (Fig 8 2) In a whole piece, everywhere in the interior parts, available forces are used in binding together the constituent particles. Thus, on creating a new surface, some forces are left free to act on particles of gases and solutions around and to attract them and then hold them on the surface. This is how adsorption occurs.

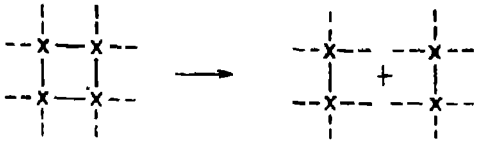
Fig 8 2 Unbalanced forces at a newly formed surface.

Types of Adsorption Adsorption on a surface ordinarily means an increase in the concentration of adsorbate at the surface relative to its concentration in the bulk phases This is called *positive adsorption.* In the case of some liquid solutions, it is observed that the solute concentrations are less in the surface layer than in the interior or bulk parts of the solution These cases are also discussed under adsorption because of the differences in concentrations: Such adsorptions are called *negative adsorptions*

If the adsorbate is held on a surface by forces of van der Waals type, the adsorption is called *van der Waals adsorption, physical adsorption* or *physisorption* If the forces holding the adsorbate are nearly as strong as experienced in usual chemical bonding, the adsorption is given the name *chemisorption, chemical adsorption* or *Langmuir 'adsorption*

All adsorptions occur with release in energy and are found to be exothermic in nature. In an adsorption process, the enthalpy change for adsorption of one mole of adsorbate on an adsorbent surface is called *enthalpy or heat of adsorption* for the particular adsorption Heat of adsorption for chemisorption is more than that for van der Waals adsorption. Heats of chemisorption are of the order of 400 kJ per mole while those for van der Waals adsorptions are about 40 kJ per mole. Table 8.1 gives a comparison of physical adsorption and chemisorption.

TABLE 8 1

Comparison between .Physical and Chemical Adsorption

	Physical adsorption	Chemical adsorption
1.	Low heats of adsorption usually in the range 20-40 kJ mol^{-1}; attraction due to van der Waals forces.	High heats of adsorption usually in the range 40-400 kJ mol^{-1}, attraction due to chemical bond forces
2.	Usually occurs at low temperatures and decreases with increasing temperature	Occurs at high temperatures.
3	Reversible.	Irreversible
4	The extent of adsorption is approximately related to the ease of liquefaction of the gas.	No correlation.
5.	Not very specific.	Often highly specific.
6.	Forms multimolecular layers.	Forms monomolecular layers.
7	Rate of increase in adsorption with pressure is much higher at higher pressure	Rate of increase in adsorption with pressure progressively decreases as pressure increases.

8.2 ADSORPTION OF GASES ON SOLIDS

The extent of adsorption of a gas on a solid depends on the following factors :

(i) The nature of the gas and of the solid.
(ii) The surface area or the specific area* of the solid.
(iii) The partial pressure of the gas in the gas phase.
(iv) The temperature of the system.
(v) The activation of the adsorbent solid.

Let us consider these points one by one.

Adsorption and Nature of Gas · Physical adsorptions are non-specific. Thus, every gas is adsorbed to a lesser or a greater extent on all solid surfaces. For a given solid surface, it is found that gases which can be condensed more easily are adsorbed to greater extents for specified values of partial pressures and temperatures Thus, adsorption of vapours is more than of permanent gases.

Chemisorptions are more specific in nature. A gas will be chemisorbed on such solids only with which it can combine chemically.

Adsorption and Nature of Adsorbent . A common example of adsorbents is charcoal It is known to adsorb strongly most of the easily liquefiable gases. Most poisonous gases belong to this type and charcoals of various types are used in gas masks.

Adsorptions of hydrogen, oxygen and nitrogen occur on metals

Adsorptions are more on porous forms of adsorbents, but the pores should be large enough to allow the diffusion of gases.

Adsorption and Pressure of the Gas : For understanding the effect of pressure on adsorption, we should note that adsorption is an equilibrium process. If the adsorbent and the adsorbate are enclosed in a closed vessel, a stage is reached when the amount of gas adsorbed equals the amount desorbed. Thus, after an initial decrease in the pressure of the gas, gas pressure as well as the amount of gas adsorbed reach constant or equilibrium values The amount of gas adsorbed depends on the surface area of the adsorbent or on its mass if the adsorbent is taken in the form of a powder. The extent of adsorption is usually expressed as x/m, where m is the mass of the adsorbent and x is the mass of the adsorbate adsorbed when adsorption equilibrium is reached. x/m can be related to the equilibrium pressure, p, of adsorbate gas. A graph drawn between x/m and p at a constant temperature is called an ***adsorption isotherm***. The simplest type of adsorption isotherm is shown in Fig 8.3. At a value p_s of equilibrium pressure, x/m reaches its maximum value and then

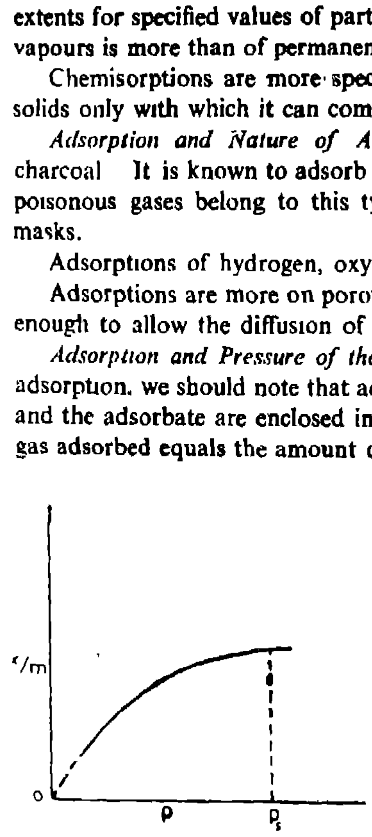

Fig. 8.3 Change in x/m with increase in gas pressure.

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*Specific area of an adsorbing solid is the surface area per gram of the adsorbent.

it remains constant even though the pressure p is increased. This state is known as *saturation state* in adsorption and p_s is called the *saturation pressure.* This type of adsorption isotherm is observed in cases where the adsorbate forms a unimolecular layer of it on the surface of the adsorbent. At low values of p the graph is nearly straight and sloping. This is expressed by the following equation :

$$\frac{x}{m} \propto p^1 \text{ or } \frac{x}{m} = \text{constant} \times p^1 \quad \ldots (8.1)$$

At high pressures x/m becomes independent of the values of p. In this range of pressures :

$$\frac{x}{m} \propto p^0 \text{ or } \frac{x}{m} = \text{constant} \times p^0 \quad \ldots\ldots\ldots (8.2)$$

In the intermediate ranges of pressure, x/m will depend on p raised to powers between 1 and 0 or fractions. For a small range of pressure values we can write .

$$\frac{x}{m} \propto p^{\frac{1}{n}} \text{ or } \frac{x}{m} = kp^{\frac{1}{n}} \quad \ldots\ldots\ldots (8.3)$$

Taking logarithms on both sides of Eq 8.3, we get :

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log p \quad \ldots\ldots (8.4)$$

Accordingly a graph between log (x/m) and log p will be a straight line with an intercept on the log (x/m) axis equal to log k and the slope of the line equal to 1/n (Fig 8 4) The equations 8.3 and 8 4 and the corresponding graphs shown in Figs. 8.3 and 8.4 are different expressions of *Freundlich adsorption isotherms.*

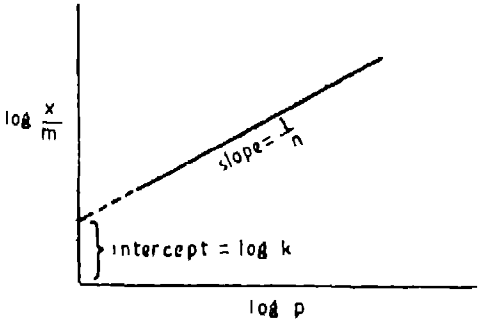


Fig. 8 4 Linear graph between $\log\frac{x}{m}$ and $\log p$.

Adsorption and Temperature of the System According to Le Chatelier principle applied to equilibrium states, if in a dynamic equilibrium process, forward change (adsorption) takes place with evolution of heat (exothermic) and a reverse change (desorption) takes place with absorption of heat (endothermic), a rise in temperature will favour the endothermic process. This argument shows that with rise in temperature adsorption should decrease. A graph drawn between amount adsorbed (x/m) and temperature (t) at a constant equilibrium pressure of adsorbate gas is called an *adsorption isobar*. Adsorption isobars of physical adsorption and chemisorption show one

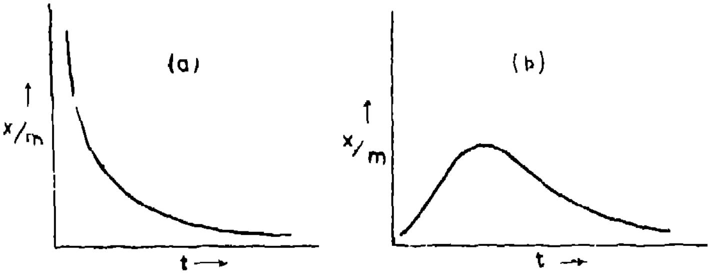


Fig 8 5 Adsorption isobars (a) Physical adsorption, (b) Chemisorption

important difference (Fig 8 5) and this difference is used for experimentally distinguishing chemisorption from physical adsorption While the physical adsorption isobar shows a decrease in x/m all along the rise in temperature, the chemisorption isobar shows an initial increase with temperature and then the expected decrease The initial increase shows that, like chemical reactions, chemisorption also needs activation energy

Activation of an Adsorbent · It is an attempt at increasing the adsorbing power of an adsorbent. One way of doing it is to increase the specific area of the adsorbent This is attained by making the surface of the adsorbent rough. This may be done by mechanical rubbing, by chemical actions or by depositing finely dispersed metals by electroplating. The other method is to subdivide the adsorbent into smaller pieces or grains. The latter method has a practical limitation Too fine a powder will make the penetration of gas difficult and, hence, it will start obstructing adsorption.

Most manufacturers keep their methods of making active adsorbents well guarded secrets. In chemisorption cases, it is not only the surface area that matters but also the extent to which valence bond forces are free The surface, edge, corner and peak atoms on an adsorbent will all have different capacities for chemisorption How a desired activity is created is an art This has to be learnt. Charcoal is activated by being heated in superheated steam.

8.3 COMPETING ADSORPTION

If we expose active charcoal in a gas mask to chlorine gas, we will find that it takes up chlorine. Before exposure to chlorine, the charcoal must be having gases contained in air adsorbed on its surface. These have been displaced by chlorine, which happens to be more adsorbable. This takes us to the two general conclusions given below.

(i) A more strongly adsorbable substance can replace an already adsorbed substance if latter is held by weaker forces.

(ii) From a mixture of adsorbates, the more adsorbable adsorbate may be adsorbed to a much greater extent than its partial pressure indicates. Thus, moisture in air, though present to a small extent, is strongly adsorbed over silica gel. Silica gel is used for drying air by adsorption of moisture. Charcoal also adsorbs polluting gases present in air in small concentration.

8.4 ADSORPTIONS FROM SOLUTIONS

Just as activated charcoal adsorbs chlorine and other poisonous gas from air in preference to oxygen and nitrogen, adsorbents adsorb certain solutes from solutions in preference to other solutes and solvents. This fact is used for adsorbing colouring matters from solutions of organic substance. Raw sugar solution is decolourized by animal charcoal. From a solution of acetic acid or oxalic acid in water, charcoal adsorbs the acids. For all these adsorptions, Freundlich adsorption isotherm relationship is found to be applicable. In place of equilibrium pressures we use the *equilibrium concentrations* of adsorbates in solutions.

$$\frac{x}{m} = k\,c^{\frac{1}{n}} \qquad \ldots\ldots(8.5)$$

$$\log\left(\frac{x}{m}\right) = \log k + \frac{1}{n}\log c$$

A graph drawn between log (x/m) and log c is found to be a straight line for small ranges of concentrations A saturation adsorption is reached at certain concentration characteristic of the adsorption-adsorbate system used.

8.5 APPLICATIONS OF ADSORPTION

The process of adsorption is widely used in the removal of undesirable colours and odours from solutions and gases. Mixtures may be separated making use of differences in adsorbabilities of components. Adsorption provides an efficient technique for concentration of substances present in very dilute solutions. Several valuable recoveries are made from industrial wastes. Softening of hard water by ion exchangers, and chromatographic techniques are based on the principle of competing adsorption. Activated charcoal is used to remove colouring matter from solutions of sugar and other organic compounds. Silica gel is particularly useful for removing moisture from air in the storage of delicate instruments which might be harmed from contact with moist air.

Adsorption measurements have been used for measuring surface areas of powders and rough surfaces.

8.6 ROLE OF ADSORPTION IN CATALYTIC REACTION

Adsorption is particularly important in catalytic activity. Many gaseous reactions proceed reapidly in the presence of suitable solid catalysts. This is because of adsorption of the reactants on the surface of the catalyst Granular forms of catalysts are more effective due to their larger adsorbing areas.

There are many gaseous reactions of industrial importance involving the use of solid catalysts. Some examples are : (i) methanol is produced by the reaction of CO and H_2 using $ZnO-Cr_2O_3$ catalyst, (ii) SO_3 is formed from SO_2 and O_2 by contact process using platinized asbestos and vanadium pentoxide as catalysts, and (iii) manufacture of ammonia by Haber's process is based on the use of iron as a catalyst.

Adsorption provides the following aids for the catalyzed reaction :

(i) Adsorption of a reactant molecule makes attack of other molecules on it easier. The adsorbed molecule is not free to move about and escape collisions.

(ii) Adsorbed molecule may expose a more vulnerable part for reaction with other molecules.

(iii) Adsorbed molecule may be dissociated to form active atoms or free radicals which react much faster than molecules. It is true for the reactions of hydrogen which splits into atoms during adsorption on metals like nickel and platinum.

(iv) Simultaneous adsorption of reactants also provides increased concentration condition. Reactions proceed more rapidly at higher concentrations of reactants.

(v) Adsorption, specially chemisorption, provides activation energy due to heat of adsorption evolved in the process.

8.7 COLLOIDAL STATE

Colloidal soutions are intermediate between true solutions and suspensions. The diameters of colloidal particles may range from 1 to 100 nm Their unique properties are due to the small size of particles. As a result, the colloidal particles may not settle down under the force of gravity even on long keeping. Ordinary suspended particles settle down sooner or later. Compared to molecular solutes, colloidal particles have much slower rates of diffusion Practically all substances can be made to exist as colloidal particles and the earlier classification of substances as crystalloids and colloids is now regarded as unnecessary.

A colloidal system is always heterogenous and consists of at least two phases : the *disperse phase* (the phase constituting the colloidal particles), and the *dispersion medium* (the medium in which these colloidal particles are dispersed). In a colloidal solution, each particle is contained within its own boundary surfaces which separate it from the continuous dispersion medium. In a true solution, the solute and the solvent form one phase in which their respective small molecules are randomly mixed.

The total surface area of the colloid particles in a colloidal solution is very large. Let us consider a solid lump of the size of one centimetre cube. Its 6 faces have a surface area of only 6 square centimetres. When the same lump is broken down to particles of millimicron (10^{-9}m) cube size, the total surface area becomes 6,000 square metres. So large surface area of particles derived from the single original cube, having only 6 square centimetres of surface, represents a large increase in the surface to volume ratio. Under this condition, adsorption by colloidal particles assumes great importance.

8.8 CLASSIFICATIONS OF COLLOIDAL DISPERSION

The colloidal solutions are frequently classified in terms of the state of the disperse phase and dispersion medium Either of these can be solid, liquid or gas. Only eight types of colloidal solutions are formed (Table 8 2). The gas-gas mixtures are always true solutions. Colloidal solutions are often also called *sols*.

TABLE 8.2
Some Common Colloidal Systems

Dispersed phase	Dispersion medium	Colloidal system	Examples
Gas	Liquid	Foam or froth	Soap suds, lemonade froth
Gas	Solid	Solid foam	Pumice stone, styrene foam, rubber
Liquid	Gas	Aerosols of liquids	Fog, clouds, insecticide sprays
Liquid	Liquid	Emulsions	Milk, emulsified oils and medicines
Liquid	Solid	Gels	Cheese, butter, boot polish, table jellies
Solid	Gas	Aerosols of solids	Smoke, dust-storm
Solid	Liquid	Sols	Most paints, starch dispersed in water, gold sol, muddy water
Solid	Solid	Solid sols	Black diamonds, minerals, ruby glass, gem stones

Based on the nature of dispersion media, colloids are sometimes grouped as hydrosols (in water), alcosols (in alcohol), benzosols (in benzene), aerosols (in air), etc.

Colloidal dispersions may also be classified as lyophobic (solvent-hating) and lyophilic (solvent-loving) sols. If water is the dispersion medium, the terms used are hydrophobic and hydrophilic sols respectively. Lyophobic sols are relatively less stable compared to the lyophilic sols. Such sols are easily precipitated (or coagulated) on the addition of small amounts of electrolytes, by heating or agitation Further, these sols are irreversible. Their coagulated masses cannot be brought back into the colloidal state by merely shaking them up with the dispersion media. Examples of lyophobic sols include sols of metals, and their insoluble compounds like sulphides and oxides Lyophobic sols need stabilizing agents to preserve them. On the other hand, lyophilic sols are self-stabilized because of strong attractive forces operating between the two phases. They are reversible sols. The solids obtained after their evaporation may be reconverted to the sol state by simply agitating them with the dispersion medium. Examples of lyophilic sols include sols of proteins in water solution and of certain high polymers in organic solvents.

8.9 MULTIMOLECULAR, MACROMOLECULAR AND ASSOCIATED COLLOIDS

It is convenient to distinguish between multimolecular and macromolecular colloids. In the colloidal solutions of the first type, the colloidal particles consist of aggregates of atoms or small molecules with diameters of less than 1 nm. For example, a gold sol may contain particles of various sizes having several atoms. Sulphur sol consists of particles containing a thousand or so of S_8-sulphur molecules. These are held together by van der Waals forces.

In the macromolecular type of colloids, the dispersed particles are themselves large molecules. These are called *macromolecules* They have very high molecular masses (from thousands to millions) Macromolecular substances are usually polymers Examples of naturally occurring macromolecules are starch, cellulose and proteins. There are many types of man-made macromolecules also such as polyethylene, nylon, polystyrene, synthetic rubber, etc. Their molecules have large sizes and contain large number of atoms, too. Since these molecules have dimensions comparable to those of colloidal particles, their dispersions are called macromolecular colloids. These dispersions resemble true solutions in some ways.

There is yet another type of colloids which behave as normal, strong electrolytes at low concentrations, but at higher concentrations exhibit colloidal state properties consistent due to the formation of aggregated particles. These are known as *micelles* Such substances are referred to as *associated colloids* Surface active agents such as soaps and the synthetic detergents belong to this class They are capable of forming ions One or both species of ions formed may have colloidal dimensions. These substances consist of organic molecules with lyophilic as well as lyophobic parts These associate together to form micelles The micelles may contain as many as 100 molecules or more. Sodium stearate ($C_{17}H_{35}COONa$) is an example of associated colloids. On dissolving in water it gives sodium and stearate ions. The stearate ions ($C_{17}H_{35}COO^-$) associate to form an ionic micelles of colloidal size.

8 10 PREPARATION OF COLLOIDAL SOLUTIONS

Lyophilic and lyophobic colloids are generally prepared by different types of methods

Lyophobic Sols

Lyophobic sols are prepared by two types of methods . (i) Condensation methods, and (ii) Dispersion methods.

CONDENSATION METHODS · These methods are based on the essential principle that the materials from which the colloidal sized particles are made are initially present as small ions or molecules. These ions or molecules are induced to combine together to form aggregates of colloidal size but not larger. Methods used may be based on chemical reactions producing insoluble products or physical changes leading to a graded and slow separation of an insoluble form of substances Some examples follow.

Chemical Methods

Oxidation · An aqueous solution of H_2S and H_2Se may be oxidized by bubbling oxygen or adding sulphur dioxide solution. Sulphur or selenium thus separated may form a sol, if the concentrations of solutions are carefully selected.

Reduction Sols of some metals like silver, gold and platinum are prepared by the reduction of their compounds soluble in water, using reducing agents like formaldehyde and hydrazine

Hydrolysis : This method is used to prepare sols of hydrous oxides of weakly electro-positive metals like iron, aluminium, tin, thorium, etc. Ferric hydroxide sol is easily obtained by pouring a dilute solution of ferric chloride into boiling water and continuing the boiling for some time

Double Decomposition : Sols of silver halides are obtained by mixing dilute solutions of silver salts and alkali halides in equivalent amounts An orange coloured arsenius sulphide sol is formed by mixing water saturated with hydrogen sulphide and a dilute solution of arsenious oxide Silicic acid sol is generally prepared by a double decomposition reaction between dilute solutions of sodium silicate and hydrochloric acid.

Physical Method

Exchange of Solvent Colloidal solutions of many substances can be prepared by pouring the solution of the substance in a suitable solvent into another solvent in which the substance is insoluble but the first solvent is miscible. For example, if an alcoholic solution of sulphur or phosphorus is rapidly mixed with water, a colloidal solution is obtained. Such sols are usually unstable

DISPERSION METHODS In these methods, lumps of the substance are broken into particles of colloidal size in presence of the dispersion medium by suitable mechanical means The sol is stabilized with some suitable stabilizer. The required dispersion may be carried out in any of the following ways.

Mechanical Disintegration . In this method, colloid mill, ball mill, or ultrasonic disintegrator are used for preparing colloidal solutions

Electrical Disintegration . In this process, dispersion as well as condensation steps are involved. Sols of metals may be prepared by striking an electric arc between electrodes of the relevant metal immersed in the liquid medium. The high temperature of the arc vapourizes some of the metal, which then condenses to form colloidal sized particles (Fig 8.6).

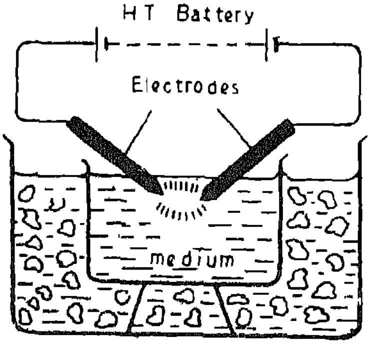


Fig. 8 6 Bredig's arc method.

Peptization : In some substances particles of colloidal size are held together weakly in the bulk form of the substance. This is Very much true of freshly formed precipitates. Such a substance can be easily dispersed by shaking it up with the dispersion medium. This process is called *peptization.* Addition of peptizing agents helps the process. Ionic compounds are peptized by electrolytes having an ion common with the disperse phase.

Lyophilic Sols

Lyophilic sols can be prepared when the material to be dispersed is brought in contact with or warmed with suitable dispersion medium. For example, **gelatin,** gum arabic, starch, egg albumin, glycogen and soaps are *peptized* by water.

Cellulose nitrate is peptized by various organic solvents, e.g. a mixture of ethanol and ether. The product obtained is commercially called 'collodion'.

8.11 PURIFICATION OF COLLOIDAL SOLUTIONS

The colloidal solutions prepared by the above methods invariably contain impurities of electrolytes and other soluble substances. Large amounts of electrolytes destabilize sols. Their removal is often called for. An important method of removing soluble impurities of sols is called *dialysis.*

Dialysis : Purification of a sol by this method is based on the fact that particles of colloidal size cannot pass through prachment paper or cellophane membranes. Small molecules and ions can pass through these membranes. A bag made from the membrane is filled with the colloidal solution and it is suspended in fresh water. To increase the rate of dialysis, warm water may be used. Movement of ions across the membrane can be made faster by putting two electrodes in water outside the membrane. An electric field of appropriate strength is applied (Fig 8.7). This modified dialysis is known as *electrodialysis.*

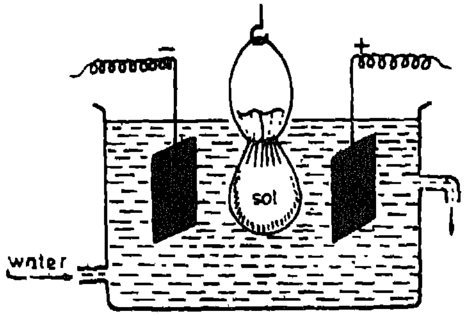


Fig. 8.7 Electrodialysis.

Ultrafiltration . Now it is possible to have treated filter papers and porous pots which permit passing out of solutions of ordinary solutes but retain colloidal particles. Such filters are called *ultrafilters.* Increased pressure or suction is required to force liquids through the small pores, while the sol prticles are retained.

8.12 PROPERTIES OF COLLOIDAL SOLUTIONS

The characteristics of colloidal dispersions may be described under various heads.

Colligative Properties : Osmotic pressures, freezing point depressions and boiling point elevations caused by colloidal dispersions are quite small. Due to high average molecular masses of colloidal particles, they give very low mole fractions in colloidal solutions. Only the osmotic pressures have measurable values. Osmotic pressure measurements can be used to determine the average molecular masses of colloidal particles.

Mechanical Properties : Three important mechanical properties of colloidal dispersions are described below.

Brownian Movement : Colloidal particles in suspension are constantly moving about in zig-zag paths (Fig 8.8). This type of erratic motion is due to the moving molecules of the dispersion medium constantly colliding with the colloidal particles. They impart momentum to colloidal particles. This random and continuing motion of colloidal particles in a dispersion medium is called *Brownian movement or motion.* **It was named after the English Botanist, Robert Brown,** who observed and investigated in 1827 a strange and interesting motion of small pieces of pollen grains suspended in water under a microscope. It was also observed that not only pollen grain pieces but small particles of coal, dust and minerals showed similar behaviour This movement is a strong evidence in support of the kinetic-molecular theory of liquids and gases. Brownian movement of very small particles is very fast but they cannot be seen In case of heavy particles, it is too slow to be seen Colloidal particles have convenient masses to exhibit Brownian movement.

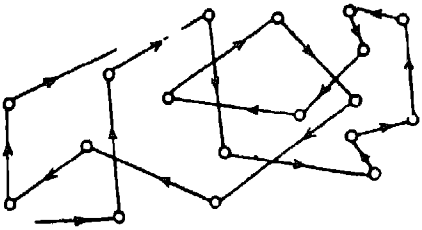


Fig 8 8 The illustration for the pattern of Brownian movement

Diffusion . Like solute particles, colloidal particles diffuse from a region of higher to a region of lower concentration. Diffusion is closely related to Brownian motion The slower motion of colloidal particles results in a much lower rate of diffusion. This process can be used to separate colloids of different sizes and also to determine their sizes.

Sedimentation : Colloidal particles tend to settle down very slowly under the influence of gravity. The rate of sedimentation can be increased to a large extent by the use of a high speed centrifuge known as *ultracentrifuge.*

Optical Properties · When a beam of light is passed through a true solution, the path of the beam through the solution is not visible But, if the light is passed through a sol, its path becomes visible, just as a beam of sunlight is seen as it enters a darkened room through a partly opened door or a slit in a curtain This phenomenon is known as the *Tyndall effect* after the name of its discoverer. It provides an easy means to demonstrate the presence of colloidal particles ((Fig 8 9.).

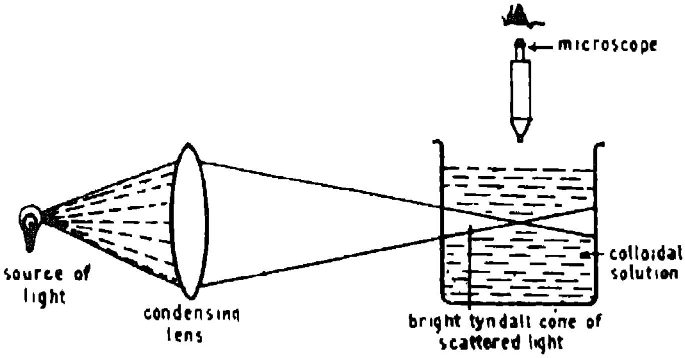
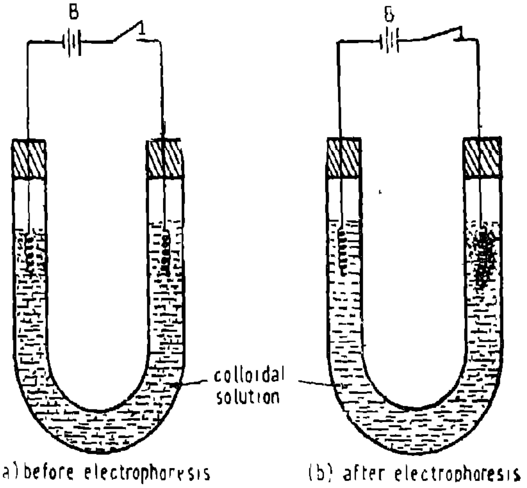


Fig 8 9 **Tyndall effect.**

Electrical Properties . Colloidal particles in most dispersions move either towards the cathode or the anode when an electric field is applied to the dispersion (Fig. 8.10).

This movement of colloidal particles under applied electric field is called ***electrophoresis***. All particles in a given colloidal solution carry the same type of charge. Thus, particles in some colloidal solutions are positively charged and in others, negatively charged. Colloidal particles can acquire this charge in any one of the ways stated here. However, colloidal solutions show an overall electroneutrality.



(a) before electrophoresis (b) after electrophoresis

Fig. 8.10 An experimental set-up for electrophoresis.

The reasons for the electrical charge of colloidal particles are given below.

(i) *Frictional electrification* due to a rubbing of particles with molecules of gaseous or liquid media.

(ii) *Electron capture* by particles from air and during electrodispersion in Bredig's arc method.

(iii) *Preferential adsorption of ions from solutions* An ionic colloid adsorbs ions common to its own lattice structure. Thus AgCl particles can adsorb Cl^- ions from chloride solutions and Ag^+ ions from solutions having silver ions. The sol will be negatively charged in the first case and positively charged in the second case.

(iv) *Dissociation of surface molecules*. Soaps expel alkali ions to acquire a negative charge Dye particles can dissociate to put into solution positive or negative ions according to composition.

(v) *Dissociation of molecular electrolytes adsorbed on the surface of particles*. H_2S molecules get adsorbed on sulphides during precipitation. By dissociation of H_2S, hydrogen ions are lost and the colloidal particles become negatively charged.

The consequences of electrical charge on colloidal particles are given below.

(i) *Charged colloidal particles.* These make colloidal solutions somewhat better electrical conductors than the dispersion media in pure state.

(ii) *Electrophoresis:* The movement of colloidal particles under an applied electric field, or electrophoresis, is due to the charge on the particles. It forms the basis of **electrodeposition** of colloids. Rubber gloves and other intricate rubber articles are made by electroplating moulds with rubber from rubber sol.

Colloids in sewage water are also removed by electroplating method. Colloidal ash particles in chimney gases are removed by passing them between high voltage plates. This is made use of in *Cottrell smoke precipitators.*

(iii) *Coagulation of sols by electrolytes:* Small concentrations of appropriate electrolytes make sols of ionic precipitates stable. However somewhat larger concentrations of electrolytes, in general, cause the colloidal particles to lose their charge and to aggregate together to form a precipitate. Precipitation of a colloid through induced aggregation of its particles in general is known as *coagulation* It has been experimentally shown that coagulation of a sol by an electrolyte does not take place until a certain minimum concentration of the added electrolyte is reached in the solution. The minimum concentration of an electrolyte in millimoles per litre of mixed solution, required to cause a coagulation of a particular sol is called the coagulation or precipitation value of the electrolyte for the sol. The coagulation values of some electrolytes for a negatively charged arsenious sulphide sol are shown in Table 8.3.

TABLE 8 3

Minimum Concentrations of Various Electrolytes Required to Cause Coagulation of Arsenious Sulphide Sol

Electrolyte	Positive ion	Concentration (mol/litre)
KCl	K^+	0 05
NaCl	Na^+	0,05
K_2SO_4	K^+	0 066
$BaCl_2$	Ba^{2+}	0 00069
$MgCl_2$	Mg^{2+}	0.00072
$Al(NO_3)_3$	Al^{3+}	0 000095

Many experiments have been carried out on the coagulation effects of electrolyte on different sols. Two main observations are ·

(i) The ions carrying charge opposite to that of colloidal particles are effective in causing coagulation of a sol.

(ii) Coagulation efficiencies of electrolytes increase considerably with increase in valence of the ion causing coagulation.

These observations together are known as *Hardy-Schulze rule.* Coagulation of sols can also be brought about by the application of an electric field or by heating.

Interactions between Colloids: Certain lyophobic colloids cause mutual coagulation on being mixed together. This occurs mainly due to neutralization of electrical charges of opposite kinds Another cause can be a neutral destruction of each other's stabilizing agents. This can happen between similarly charged colloids also.

Certain lyophilic colloids are known to exert a protecting influence on lyophobic colloids against their coagulation by electrolytes. Thus, a silver sol protected by hydrolyzed proteins or a gold sol protected by **gelatin**, gum or starch may not be easily coagulated. A term *gold number*, defined as follows, is used for grading the protective powers of colloids

Gold number of a protective colloid is the minimum number of milligrams of the dry colloid which, when present in 10 ml of standard red gold sol, will just prevent the change of colour to blue on addition of 1 ml of a 10% NaCl solution.

8.13 EMULSIONS

Emulsions are liquid-liquid colloidal dispersions. Common examples of emulsions are milk and mayonnaise. Both of these consist of small drops of liquid fat dispersed in an aqueous medium. The process of making an emulsion is termed *emulsification*. Emulsions can be of two types, the *oil-in water type* and the *water-in oil type*. In the first type of emulsions, disperse phase consists of small droplets of oil dispersed in water Water-in oil type of emulsions consist of water droplets dispersed in a continuous medium of oil The droplets in emulsions can be somewhat larger than the usual particles found in sols

Emulsifying Agents : Emulsions may be produced by vigorously agitating a mixture of the liquids, or better by subjecting the mixture to ultrasonic vibrations. Emulsions are generally unstable unless a third stabilizing substance, known as *emulsifying agent* is also present. In the absence of an emulsifying agent, the dispersed droplets coalesce together and eventually the emulsion breaks up into two layers. The most frequently employed emulsifying agents are soaps and detergents which coat the droplets and obstruct aggregation of droplets. Other stabilizing agents include proteins, gum, agar, etc The emulsifying properties of soaps and detergents are of great significance in washing of clothes and crockery. They emulsify the greese and carry it away in the wash water along with dirt and dust adhering to greese.

The digestion of fats in the intestines is aided by emulsification. A little of the fat forms a sodium soap with the alkaline solution of the intestine, and this soap emulsifies the rest of the fat, thus making it easier for the digestive enzymes to carry out their metabolic functions. In pharmaceuticals and cosmetics, various lotions, creams and ointments, and a large number of other preparations are emulsions of oil-in-water or water-in-oil type. Several oily drugs are prepared in the form of emulsions.

Emulsions find many industrial applications. For concentrating the ore, the finely pulverized ore is treated with an oil emulsion and foams in such a way that the particles of the desired mineral are carried to the surface, where they are collected.

Emulsions are sometimes objectionable, e.g. in oil wells which give petroleum emulsified with water. Emulsions may be broken down (demulsified) to yield constituent liquids by physical methods such as freezing, boiling, filtration, electrostatic precipitation or by centrifugation, and by chemical methods which destroy the emulsifying agents. Cream is separated from milk by the centrifugation method.

EXERCISES

8.1 Explain the terms 'colloidal solution' and 'colloidal state'. How are colloids classified on the basis of (a Physical states of components, (b) Nature of dispersion medium, (c) Attractions between disperse phase and dispersion medium.

8.2 What is the difference between multimolecular and macromolecular colloids ? Give at least three examples of each of them. What are associated colloids and in what way do they differ from the other two types of colloids ?

8.3 What are the different methods employed for the preparation of colloids ? How are they purified ? How may we get colloidal solutions of the following in water : (i) Sulphur, (ii) $BaSO_4$, (iii) Silver ?

8.4. What are the basic differences between true molecular solutions and colloidal solutions ? Describe the possible origins of electric charge on colloidal particles.

8.5 Explain what is observed when

(a) a beam of light is passed through a colloidal solution of arsenious sulphide.
(b) sodium chloride is added to a ferric hydroxide solutions
(c) an electric current is passed through a colloidal solution.

8.6 Colloidal arsenious sulphide sol is readily precipitated by a small amount of aluminium chloride, it is also precipitated by about seven times the amount of barium chloride, and by several hundred times as much concentration of sodium chloride. Discuss the significance of these observations and state the rule based on them.

8.7 What do you understand by the term 'electrophoresis' and how would you demonstrate this phenomenon ?

8.8 Explain the following terms

(i) Tyndall effect
(ii) Brownian movement
(iii) Sedimentation
(iv) Coagulation

8.9 Write essays on :

(i) Adsorption
(ii) Emulsions

8.10 Write short notes on :

(i) Hardy-Schulze rule
(ii) Peptization

8.11 Differentiate between physical and chemical adsorptions.

8.12 What do you mean by an adsorption isotherm and an adsorption isobar. Explain Freundlich adsorption isotherm for the adsorption of gases on solids.

8.13 Describe the role of adsorption in catalytic reactions.

8.14 Write notes on :

(i) desorption, (ii) demulsification, (iii) precipitation powers, and (iv) gold numbers.

UNIT 9

The Oxygen Family (Group VIA Elements)

We have already studied group I A to V A elements. In the present unit we shall study about group VI A elements.

9.1 THE FAMILY CHARACTERISTICS

The elements oxygen, sulphur, selenium, tellurium and polonium constitute group VIA of the Periodic Table They are elements of the p-block with ns^2np^4 valency shell electronic configurations Oxygen is the most abundant element on earth It constitutes 46 6 % of the earth's crust It is an important constituent of our atmosphere. About 21 % by volume of the atmosphere is oxygen. Sulphur occurs only to the extent of 0 052% in the earth's crust It is found as insoluble sulphides in primary rocks and as soluble sulphates in secondary rocks. It also occurs in free state, chiefly in volcanic areas The other elements of this group are comparatively rare.

As with elements of Groups IVA and VA, the non-metallic characteristics in this group also diminish gradually as we move down the group The first three elements are non-metals They are referred to as *chalcogens* (ore forming elements), because many common ores of metals are either oxides or sulphides. Tellurium is more non-metallic and polonium more metallic in character Polonium is a short lived radioactive element

You already know that as we go down a group the ionic radii increase. Further, the VIA group being at the right end side of the Periodic Table, the elements of the group are characterized by high ionization energies which decrease as we go down the group The density of the elements increase from sulphur to polonium. The elements are also characterized by relatively high electronegativity values which decrease down the group along with a decrease in non-metallic character. The electronic configurations and general trends in properties of the elements are summarized in Table 9 1

All the elements have ns^2 np^4 outer electonic configurations of atoms. They try to attain the noble gas configuration by gaining or sharing electrons. Oxygen with its high electronegativity value tends to complete its octet by gaining two electrons. Thus, most metal oxides are ionic and contain O^{2-} ions. Oxygen exhibits the -2 oxidation state. The electronegativities of the other elements are much less. Hence, there is a

TABLE 9 1

Properties of Elements of Oxygen Family

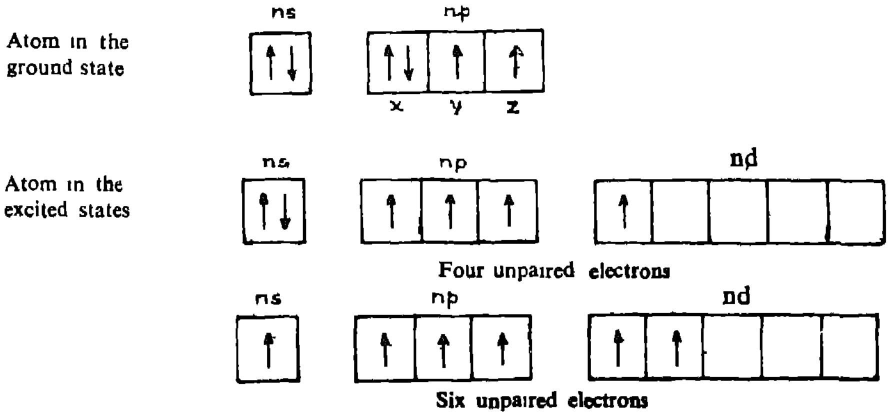
Element	Abundance in earth's crust (ppm)	Atomic number	Electronic configuration	Ionic radius, (Å)	b p (K)	m p (K)	Density in the solid state (g cm^{-3})	Electronegativity	Ionization energy (kJ mol^{-1})	Oxidation state
O	466,000	8	[He] $2s^2 2p^4$	1.40	90	55	1.14	3.50	1314	-2
S	520	16	[Ne] $3s^2 3p^4$	1.85	718	392*m**	2.07	2.50	1000	$-2, +2, +4, +6$
Se	0.09	34	[Ar] $3d^{10} 4s^2 4p^4$	1.98	958	490*g***	4.79	2.40	941	$-2, +2, +4, +6$
Te	0.002	52	[Kr] $4d^{10} 5s^2 5p^4$	2.21	1263	723	6.25	2.00	869	$-2, +2, +4, +6$
Po	—	84	[Xe] $4f^{14} 5d^{10} 6s^2 6p^4$	—	1235	527	9.4	1.75	—	$+2, +4$

**m* stands for monoclinic

***g* stands for grey

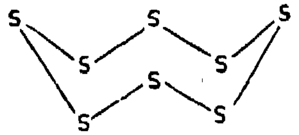
very low probability for them to form dinegative ions. The tendency for the -2 oxidation state diminishes from sulphur downwards This is reflected in the instability of the hydrides. The hydride of polonium, H_2Po, is very unstable.

For oxygen the -2 oxidation state alone is predominant (exceptions H_2O_2 and OF_2. The other elements show additional oxidation states of $+2$, $+4$ and $+6$. This is due to the presence of vacant *d* orbitals in these elements.



The oxygen molecule is diatomic. Under normal conditions oxygen exists as a gas. The molecules of other elements have larger atomicities and they exist as

solids. Thus, sulphur has 8 atoms per molecule which are arranged in the form of a puckered ring.



S_8 molecule

Oxygen to a limited extent and sulphur to a larger extent exhibit the property of *catenation*. Thus. compounds of the type H–O–O–H, H–S–S–H, and H–S–S–S–H, are known.

All the elements of the group exhibit *allotropy*. Thus, oxygen exists as O_2 and O_3 (ozone). Sulphur has a number of allotropes like rhombic (α), monoclinic (β), and plastic (γ) sulphur. Selenium, tellurium and polonium also show allotropy.

9.2 ANOMALOUS BEHAVIOUR OF OXYGEN

The first members of the groups show anomalous behaviour and so does oxygen. Thus, while oxygen is a gas the other elements of the group are all solids. Oxygen molecule is diatomic, but the molecules of the other elements are polyatomic. Oxygen shows an oxidation state of –2 while the other elements show additional oxidation states also

9.3 COMPOUNDS

Hydrides · All elements of this group form volatile hydrides of the type H_2R. The stability of the hydrides diminishes from oxygen to polonium. While water is an odourless liquid, the other hydrides are offensive smelling gases at ordinary temperatures. The liquid character of water and its other anomalous properties are due to hydrogen bonding in it

All hydrides, except water, are reducing agents and are weakly acidic. The first two members of the group also give hydrides of the type H_2R_2 (H_2O_2 and H_2S_2). While H_2O_2 is somewhat stable, H_2S_2 is very unstable.

Halides The elements of this group form a variety of halides. A few typical halides are indicated in Table 9.2.

TABLE 9.2

Halides of Elements of Oxygen Family

Element	Fluorides	Chlorides	Bromides	Iodides
O	OF_2	Cl_2O, ClO_2 Cl_2O_7	Br_2O	I_2O_5
S	S_2F_2,SF_4,SF_6	S_2Cl_2,SCl_2	S_2Br_2	—
Se	Se_2F_2,SeF_4,SeF_6	Se_2Cl_2,$SeCl_4$	$SeBr_2$,$SeBr_4$	—
Te	TeF_4,TeF_6	$TeCl_2$,$TeCl_4$	$TeBr_2$,$TeBr_4$	TeI_4
Po		$PoCl_2$,$PoCl_4$	$PoBr_2$,$PoBr_4$	PoI_4

The maximum valency of 6 is shown in the hexafluorides. These are formed by sp^3d^2 hybridization and have octahedral structures.

Oxides: All elements of this group give dioxides. The dioxides are obtained by burning the elements in air.

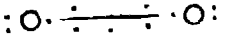
The best known trioxide is SO_3. It is obtained by the catalytic oxidation of SO_2.

9.4 STRUCTURE OF OXYGEN MOLECULE

Representation of oxygen molecule as:

$$:\ddot{O}::\ddot{O}:$$

fails to account for the paramagnetism of oxygen (cf. page 52, Part I). So, a structure in which the two oxygen atoms are joined by a covalent bond and by two 3-electron bonds is suggested.



[The paramagnetic character of oxygen can be explained in a better way by studying molecular orbital structure of oxygen molecule (see p. 25 Unit 4)]

9.5 OZONE

Ozone (O_3) is an endothermic compound i.e. when ozone is formed heat is absorbed. It can be obtained by the action of ultraviolet rays on oxygen. So, some ozone is usually formed at heights of about 20 kilometers above the surface of the earth. The ozone layer protects the earth's surface from an excessive penetration of the harmful ultraviolet rays. Ozone is, however, too reactive to be found in air at ground level. Being another form of oxygen it may be regarded as the allotrope of the former.

Preparation. If a slow stream of *dry* oxygen is subjected to a *silent* electric discharge in an ozonizer (Fig 9.1), 10% conversion of the oxygen into ozone can take place

$$3O_2(g) \rightleftharpoons 2O_3(g);\ \Delta H = +142\ \text{kJ/mol of ozone formed}$$

Since ozone is an endothermic compound, it is necessary to use a silent electric discharge, otherwise sparking would generate heat and decompose it.

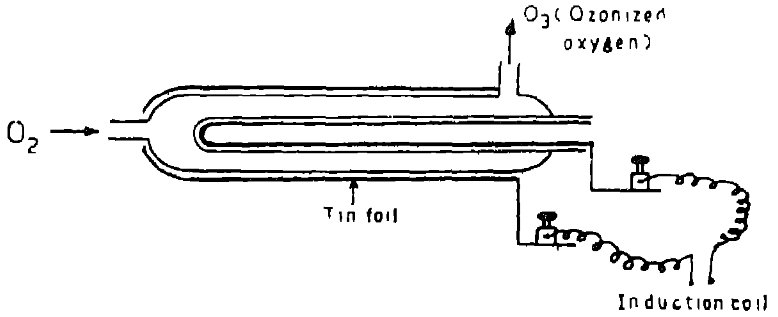


Fig. 9.1 Preparation of ozone.

Properties: Ozone is a pale blue gas. It has a characteristic smell. Being an endothermic compound it is unstable and reactive.

Ozone is a more powerful oxidizing agent than molecular oxygen. It oxidizes lead sulphide to lead sulphate, iodide ions to iodine, and ferrous ions (Fe^{2+}) to ferric ions (Fe^{3+}).

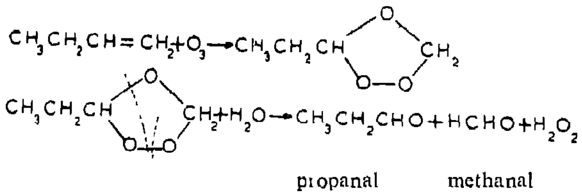
$$PbS + 4O_3 \longrightarrow PbSO_4 + 4O_2$$

$$2I^- + H_2O + O_3 \longrightarrow I_2 + 2OH^- + O_2$$

$$2Fe^{2+} + 2H^+ + O_3 \longrightarrow 2Fe^{3+} + H_2O + O_2$$

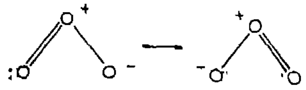
Ozone is a mild bleaching agent and a strong sterilizing agent for water and air

Ozone attacks organic compounds having carbon-carbon double bonds to give ozonides These, on hydrolysis, give aldehydes and ketones. The reaction known as ozonolysis is useful in fixing the position of the double bonds in organic molecules.



In the presence of ozone, mercury is oxidized to a suboxide It starts sticking to glass and loses mobility This is termed as the *tailing* of mercury and is used as a test for ozone.

Structure: Ozone is considered as a resonance hybrid between the two structures shown below



Uses. Ozone is used (i) for sterilization of water, (ii) in the purification of air in crowded theatres and in underground railways, (iii) as a mild bleaching agent, and (iv) for ozonolysis of organic compounds.

9.6 SULPHURIC ACID

Sulphuric acid is the most common oxy-acid of sulphur It is a very important industrial chemical. Its manufacture is based on the catalytic oxidation of sulphur dioxide The combination between oxygen and sulphur dioxide is slow, reversible, and is an exothermic process

$$2SO_2 + O_2 \rightleftharpoons 2SO_3;\ \Delta H = -98\text{kJ/mol of } SO_3$$

To obtain a fairly high yield of SO_3, low temperature, high pressure, and excess of oxygen are necessary (Le Chatelier's principle). The optimum conditions used in the manufacture of sulphuric acid by the *contact process* are : (i) use of a catalyst, vanadium pentoxide, (ii) an optimum working temperature of 723K, and (iii) an excess of air

The Contact Process The flow diagram for the manufacture of sulphuric acid by the contact process is shown in Fig. 9 2

The burner gases from the sulphur or pyrite burners always contain impurities like As_2O_3, sulphur or pyrites dust, and sulphuric acid fog These impurities, if not removed, result in the poisoning of the catalyst.

For their removal, these gases are first passed through a *dusting tower* where heavy dust particles are made to settle down mechanically or with the help of a *Cottrell electrical precipitator*. The gases are then led through *cooling pipes* where they are washed by a down-coming spray of water. They are then dried up by a spray of concentrated H_2SO_4 coming down in a *drying tower* containing coke. The dried gases are then freed from arsenic impurities by passing them through an *arsenic purifier*, which contains gelatinous ferric hydroxide resting on shelves. The presence of dust and As_2O_3 particles in the gas is seen by passing it through a *testing box* known as Tyndall box. The use of Tyndall effect is made in this treatment. If particles are seen in the Tyndal box, the gas is sent back to precipitator.

The *contact chamber* employed in Badische process consists of an iron converter provided with iron pipes packed with vanadium pentoxide, V_2O_5 The vanadium contact mass is porous and is in the form of small pellets The gases are passed through a *preheater* where they are first heated to about 723K and then passed into the converter. As they pass through the iron pipes containing V_2O_5 catalyst plus a compound of potassium (promotor), SO_2 is oxidized to SO_3. As the reaction is exothermic, the heat produced increases the temperature of the catalyst to about 723K Hence, after the work starts, the gases are not heated in the preheater but are passed directly into the contact chamber

Platinized magnesium sulphate is also used as a catalyst in the converter, in the Grillo process.

Sulphur trioxide is passed into the *absorption tower* where it is absorbed by 98% sulphuric acid

Thus, SO_3 dissolves in the sulphuric acid forming fuming sulphuric acid or *oleum*. Oleum is an oily liquid which emits white fumes in moist air. It is used as an oxidizing agent and as a sulphonating agent in industries concerned with organic chemicals.

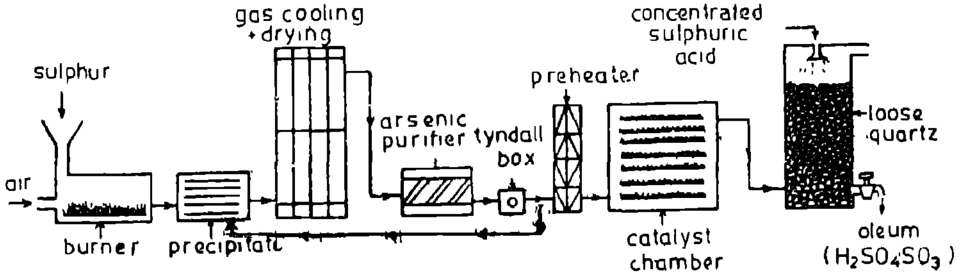
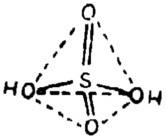


Fig 9 2 Contact process for the manufacture of sulphuric acid.

Properties · Sulphuric acid is a covalent substance Its molecule has a tetrahedral structure Sulphur is hexavalent in this compound.



Its high boiling point and high viscosity are due to the presence of hydrogen bonding which binds a number of simple molecules into clusters.

Concentrated sulphuric acid has a great affinity for water. Substances will not only give up their water of crystallization in contact with it but also lose the elements of water when a hydrogen atom and a hydroxyl group are situated near to one another.

$$C_6H_{12}O_6 \xrightarrow{\text{conc } H_2SO_4} 6C + 6H_2O$$

glucose

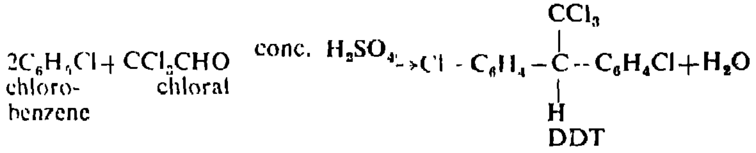
$$HCOOH \xrightarrow{\text{conc. } H_2SO_4} H_2O + CO$$

formic acid

The dehydration of organic compounds is industrially important Thus, diethyl ether is manufactured by dehydrating ethanol.

$$2C_2H_5OH \xrightarrow{\text{conc } H_2SO_4} C_2H_5-O-C_2H_5+H_2O$$

DDT is manufactured by dehydrating a mixture of chlorobenzene and trichloracetaldehyde (chloral)



$$\underset{\text{chloro-benzene}}{2C_6H_5Cl} + \underset{\text{chloral}}{CCl_3CHO} \xrightarrow{\text{conc. } H_2SO_4} \underset{\text{DDT}}{Cl-C_6H_4-\overset{\displaystyle CCl_3}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}-C_6H_4Cl} + H_2O$$

Hot concentrated sulphuric acid is an oxidizing agent as it can provide oxygen: $H_2SO_4 \rightarrow H_2O + SO_2 + [O]$ It oxidizes carbon to CO_2, phosphorus to P_2O_5, which forms H_3PO_4 with water, and several metals to their oxides which may then form sulphates if basic in nature. It is used in the preparation of acids which are more volatile than itself, but are not oxidized by it or decomposed by mild heating.

$$KNO_3 + H_2SO_4 \rightarrow HNO_3 + KHSO_4$$
$$NaCl + H_2SO_4 \rightarrow HCl + NaHSO_4$$

Uses It is mostly used as a cheaper and not too volatile an acid and a dehydrating agent Common uses are in : (i) the manufacture of fertilizers, dyes, drugs, explosives, paints, synthetic fibres and detergents; (ii) the manufacture of acids like HCl and HNO_3 (iii) metallurgy for dissolving minerals and for 'pickling' of metal surfaces (for removal of basic oxides) before further treatment, and (iv) the refining of petroleum

9.7 SODIUM SULPHITE

Sodium sulphite (Na_2SO_3) is the salt of sulphurous acid, H_2SO_3. It is used as a source of SO_2 which is a mild bleaching agent for sugar, wool and silk, a strong disinfectant for air, an antichlor, and a preservative for food-stuffs. Sodium sulphite is also used in the preparation of some photographic developers and as an antiseptic. It is added to boiler feed water to prevent scale formation and corrosion.

Preparation · It is manufactured by passing sulphur dioxide into a solution of sodium carbonate until the product has an acid reaction. The solution consisting of sodium bisulphite is boiled with more sodium carbonate until no more carbon dioxide escapes. The solution on crystallization gives crystals of $Na_2SO_3\ 7H_2O$

$$Na_2CO_3 + 2SO_2 + 2H_2O \rightarrow 2NaHSO_3 + H_2O + CO_2$$
$$2\ NaHSO_3 + Na_2CO_3 \rightarrow 2\ Na_2SO_3 + H_2O + CO_2$$

9.8 SODIUM METABISULPHITE

This product ($Na_2S_2O_5$) is used as a reducing agent in the tanning industry, as a bleaching agent, and as an antichlor in the textile industry It is also used in the manufacture of hydrosulphite solutions.

It is obtained by dehydration of sodium bisulphite by careful heating at a controlled temperature.

$$2\ NaHSO_3 \rightarrow Na_2S_2O_5 + H_2O$$

EXERCISES

9.1 Why is oxygen a gas while sulphur is a solid ?

9.2 The tendency to show the −2 oxidation state diminishes from sulphur to polonium. Why ?

9.3 While oxygen shows only divalency, the other members of the group show valencies of 4 and 6 also Explain.

9.4 Among the hydrides of oxygen family elements, water shows anomalous properties. Why ?

9.5 What is the geometry of the SF_6 molecule ?

9.6 What is the structure at present assigned to the oxygen molecule ?

9.7 How would you convert oxygen into ozonized oxygen ?

9.8 What is ozonolysis ?

9.9 What are the most favourable conditions for the conversion of SO_2 into SO_3 ?

9.10 How do you account for the high boiling point and viscosity of sulphuric acid ?

9.11 Give some examples of the industrial applications of the dehydrating property of sulphuric acid.

9.12 State the uses of sulphuric acid.

9.13 Write the electron dot formula of sulphuric acid.

9.14 How is sodium sulphite obtained ? What are its uses ?

9.15 How is sodium metabisulphite obtained from sodium bisulphite ? What are the uses of the compound ?

UNIT 10

The Halogen Family (Group VIIA Elements)

The name *halogens* is derived from Greek *halos* which means the sea salt producers. The common salt is sodium chloride and other halides are very much like it. In the Periodic Table, these elements have positions immediately before the helium group elements. They are also given the group number VIIA. The elements of this group, viz. fluorine, chlorine, bromine and iodine, occur in many places. Being soluble in water, with the passing of time all types of halides have been washed down to seas and lakes. The last element of this group, astatine, is quite rare.

10.1 FAMILY CHARACTERISTICS

The halogens are *p*-block elements having an outer electronic configuration of ns^2np^5. Atoms of these elements are one electron short of the number of electrons in atoms of noble gases which follow them in the Periodic Table. The chemistry of these elements is dominated by their tendency to complete the octet. This they can do either by taking up an electron from metals to form ionic compounds or by sharing an electron with other non-metals to form covalent compounds. They all form diatomic molecules. The halogens are the most reactive elements. They are all coloured. Fluorine is pale yellow, chlorine is yellowish green, bromine is reddish brown or orange and iodine is violet-black. This is because they absorb light in the visible range forming excited states. The intermolecular forces are very weak in halogens. They become stronger as we reach iodine. Thus, fluorine and chlorine are gases, bromine is a volatile liquid and iodine is a volatile solid.

Occurrence : The halogens being highly reactive do not occur in free state. They occur in nature only as compounds. The order of their relative abundance in the earth's crust is shown in Table 10.1. Fluorine ocurs mostly as the insoluble fluorspar (CaF_2), cryolite ($AlF_3.3NaF$) and fluoroapatite [$3Ca_3(PO_4)_2.CaF_2$]. Chlorine is present in sea water as alkali and alkaline earth chlorides. It is also present in brine wells and as rock salt deposits. Bromine too occurs in sea water as bromides. Concentration of iodides in sea water is extremely small. However, some seaweeds can take it up from the sea water and we may get as much as about 0.5% of iodine in these weeds. Chile saltpeter has about 0.2% iodine as sodium iodate, $NaIO_3$

General Trends in the Group : The electronic configurations of the halogens and the general trends in properties are summarized in Table 10.1.

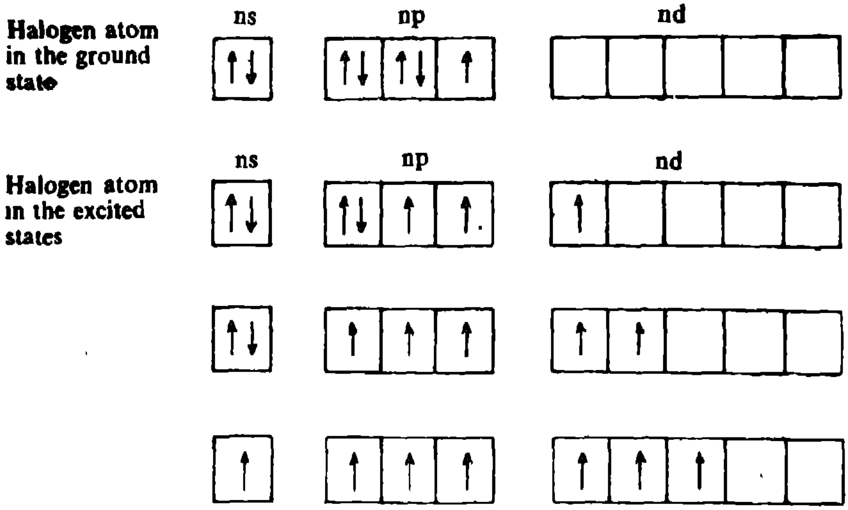
TABLE 10.1

Properties of Elements of Halogen Family

Element	Atomic number	Electronic configuration	Abundance in earth's crust (ppm)	Atomic radius (Å)	Ionic radius, X⁻ ion (Å)	Electron affinity (kJ/mol)	Electronegativity	m p (K)	b p (K)	Ionization energy kJ/mol)	Oxidation state
F	9	[He] $2s^2 2p^5$	800	0.72	1.36	333	4.0	53	85	1681	−1
Cl	17	[Ne] $3s^2 3p^5$	480	0.99	1.81	348	3.0	172	238	1255	−1, +1, +3, +5, +7
Br	35	[Ar] $3d^{10} 4s^2 4p^5$	2	1.14	1.95	340	2.8	266	332	1142	−1, +1, +3, +5, +7
I	53	[Kr] $4d^{10} 5s^2 5p^5$	0.3	1.33	2.16	297	2.5	386	456	1007	−1, +1, +3, +5, +7

Halogens show the expected periodicity in properties. The atomic and ionic radii increase steadily from fluorine to iodine. Being the elements at the right extreme of the Periodic Table, the halogens are characterized by high values of ionization energies, electron affinities and electronegativities. Because of their high ionization energies, the halogens show little tendency to lose electrons. Only iodine and, to a lesser extent, bromine form uni-positive ions. The halogens show typical non-metallic character. As expected, the non-metallic character diminishes down the group. Thus, iodine shows some metallic lustre. It can exist as cations in fused ICl

All the halogens show an oxidation state of −1. Fluorine being an element of the second period ($n = 2$), its atoms do not have *d* orbitals in the second energy shell. Hence, it does not show higher oxidation states or variable valency. The other halogens have vacant *d* orbitals available and on that account exhibit variable valency and higher oxidation states.


Halogen atom in the ground state
ns
np
nd
Halogen atom in the excited states
ns
np
nd

On account of their high electron affinities, halogens easily pick up electrons from other substances. They act as strong oxidizing agents.

All the halogens react directly with metals and to varying extents with non-metals to form halides. The reactivity of the halogens decreases down the group.

Oxidizing Action : All the halogens are strong oxidizing agents. Their actions on water and alkalies are described below:

Action on Water:Fluorine oxidizes water to oxygen and ozone.Oxygen difluoride, OF_2, and hydrogen peroxide may also be formed.)

$$2H_2O + 2F_2 \rightarrow 4HF + O_2$$

$$3H_2O + 3F_2 \rightarrow 6HF + O_3$$

Because of the formation of HF, which is itself a liquid and can absorb moisture to form liquid droplets, fluorine gives fumes on mixing with moist air.

Chlorine and bromine react less vigorously.

$$X_2 + H_2O \rightarrow HX + HOX;\ (X = \text{Cl or Br})$$

In sunlight, HOX loses oxygen and, hence, chlorine and bromine water evolve oxygen under sunlight.

$$2HOX \rightarrow 2HX + O_2$$

Iodine has very little reaction with water. It is, however, slightly soluble and forms a yellow solution. It is much more soluble in solutions containing KI due to formation of I_3^- ions.

$$I_2 + I^- \rightleftharpoons I_3^-$$

Since all the dissolved iodine is available for chemical reactions, standard solutions of iodine are made in 10% KI solution.

At low temperatures, Cl_2, Br_2 and I_2 form crystals of hydrates, $Cl_2 . 7.3\ H_2O$, $Br_2 . 10H_2O$ and $I_2.xH_2O$.

Action on Alkalies : Fluorine reacts with a 2% alkali solution to form mainly OF_2

$$2F_2 + 2OH^- \rightarrow OF_2 + H_2O + 2F^-$$

Hot concentrated alkalies yield mainly fluoride and O_2 Other halogens react with cold dilute alkalies to give the hypohalite ions (OX^-). These tend to decompose on rise in temperature and in concentrated solutions:

$$X_2 + OH^- \rightarrow OX^- + X^- + H^+$$
$$3OX^- \rightarrow XO_3^- + 2X^-$$

Estimation of Halogens . Iodine is estimated by titration with a solution of sodium thiosulphate. Freshly prepared starch solution is used as an indicator. It gives a deep blue colour with traces of iodine

$$2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$$

Colourless sodium tetrathionate and NaI are formed in the titration. Small amounts of chlorine and bromine in a solution can be accurately estimated by conversion to iodine by adding potassium iodide. The liberated iodine is titrated against $Na_2S_2O_3$.

10.2 HYDRIDES

Hydrides are of the type HX. While the reaction of hydrogen with fluorine is violent, the reaction with iodine is very slow at room temperature This is in conformity with the decreasing reactivity of halogens with increasing atomic numbers

HF and HCl are thermally stable and not easily oxidized They can be prepared by heating fluorides and chlorides with concentrated sulphuric acid

$$CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + 2HF$$
$$NaCl + H_2SO_4 \xrightarrow{\text{cold}} NaHSO_4 + HCl$$
$$NaHSO_4 + NaCl \xrightarrow{\text{heat}} Na_2SO_4 + HCl$$

HBr and HI are strong enough to reduce hot conc. H_2SO_4. Hence, they cannot be prepared by this method. Though HBr can stand some heating, HI dissociates on heating. To avoid such dissociation they are prepared by hydrolysis of the corresponding phosphorus halides with cold water.

$$PX_3 + 3H_2O \rightarrow H_3PO_3 + 3HX;\ (X = Br \text{ or } I)$$

While HCl, HBr and HI are gases, HF is a low boiling liquid (b.p. 292K). anomalous physical property of HF is due to hydrogen bonding Sec. 10.5. Hydrogen halides are covalent substances. But their aqueous solutions conduct electricity due to generation of H_3O^+ ions by interaction with water.

$$HX + H_2O \rightarrow H_3O^+ + X^-$$

10.3 POSITIVE OXIDATION STATES OF HALOGENS

It is a well established fact that within a group, the metallic character increases with increase in atomic number But in this group of highly electronegative elements development of metallic character is very slow Thus, even though iodine and, to a lesser extent, bromine show some basic properties, they act mainly as non-metals On electrolysis of fused ICl, part of iodine is liberated at the cathode Ionization can be represented as

$$2ICl \rightleftharpoons I^+ + ICl_2^-$$

In ICl_3, iodine is in the tripositive state

Compounds containing unipositive bromine are also known

Oxides and Oxyacids of Halogens : The oxides of halogens are endothermic compounds (except F_2O) and as such are unstable and liable to explode. The higher oxides and oxides of iodine are relatively more stable Because of thermodynamic and kinetic factors, oxides of bromine are the least stable. Table 10 2 lists the oxides and oxyacids of halogens Some of the unstable oxides have not been included in this Table In these oxyacids the proton responsible for acid character is present as a hydroxyl group directly attached to the halogen This is true of most oxyacids (compare H_2SO_4, HNO_3, H_3PO_4, etc.).

TABLE 10 2

Oxides and Oxyacids of Halogens

Oxidation state	Fluorine†	Chlorine		Bromine		Iodine	
+1	OF_2 (g)	Cl_2O (g)	$HOCl$*	Br_2O (g)	$HOBr$*	—	HOI
+3		—	$HOClO$*				
+4		ClO_2(g)	—			I_2O_4(s)	
+5		—	$HOClO_2$*		$HOBrO_2$	I_2O_5(s)	$HOIO_2$
+6		Cl_2O_6 (l)					
+7		Cl_2O_7 (l)	$HOClO_3$		$HOBrO_3$	I_2O_7(s)	$HOIO_3$

*Stable in solution state only †Oxidation state do not apply for fluorine.

The names of oxyacids of chlorine and their salts are as follows.

$HOCl$	Hypochlorous acid	$NaOCl$	Sodium hypochlorite
$HOClO$ or $HClO_2$	Chlorous acid	$NaOClO$ or $NaClO_2$	Sodium chlorite
$HOClO_2$ or $HClO_3$	Chloric acid	$NaOClO_2$ or $NaClO_3$	Sodium chlorate
$HOClO_3$ or $HClO_4$	Perchloric acid	$NaOClO_3$ or $NaClO_4$	Sodium perchlorate

Names in case of other halogens are similar. A more detailed study of these compounds is not possible at this stage.

Uses of Halogens · Chlorine is the cheapest halogen to prepare and is the most useful amongst them It is used for sterilizing drinking water and for bleaching cloth and paper pulp It is also used in making insecticides like DDT, germicides, dyes, drugs, plastics like PVC, and some chlorine substituted hydrocarbon solvents.

Fluorine is the strongest oxidizing agent and has been used as such in rockets. Inertness and stability of fluorocarbons has led to use of these as refrigerant gases (Freon-12, CF_2Cl_2) and in making heat resisting plastics like Teflon $(C_2F_4)_n$.

A major use of bromine is in making ethylene dibromide which is added to petrol for eliminating lead as volatile bromide Lead tetraethyl is used as an antiknock agent. If the resulting lead were not removed from the engine along with the exhaust gases, it would damage the engine Large amounts of silver bromide are used in photography Some drugs also have bromine compounds

Iodine is used as an antiseptic in the form of an alcoholic solution, tincture iodine. It also goes into making some medicines, dyes and AgI used for photographic film and cloud seeding Iodized salt containing NaI is supplied in iodine deficient areas as a protection against spread of goiter.

10.4 FLUORINE

It occurs mainly as the fluorides, fluorspar (CaF_2), and cryolite (AlF_3 3NaF).

Because of its high reactivity and its great affinity for hydrogen, the methods used for the preparation of other halogens cannot be used in the case of fluorine.

Fluorine is prepared by electrolysis of an electrolyte containing no other anion than fluoride. The potential required for the discharge of fluoride ions being the highest, other anions will be discharged at the anode in preference to the fluoride ion. Further, the electrolyte must be free from even traces of water which react rapidly with free fluorine. From water oxygen is formed before fluorine can be formed from the flouride ions A solution of KF in HF in the ratio of 1 mole to 2.5 moles is liquid at 363K and is quite convenient to use. This electrolyte gives fluorine at the anode and hydrogen at the cathode. It is essential that the two gases should not mix. For this requirement electrolysis is carried out in a V-shaped vessel of copper, nickel or steel (Fig 10.1). These metals are covered with protective layers of insoluble fluorides.

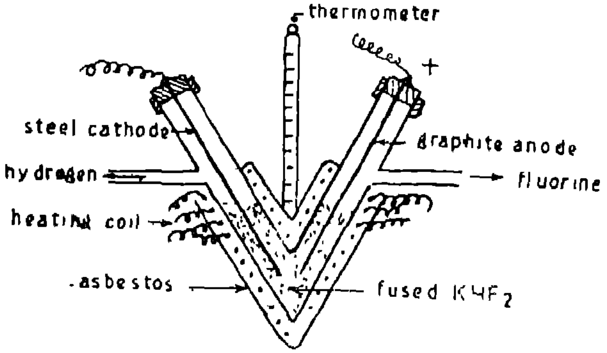


Fig. 10.1 Flourine by electrolysis of KHF_2.

Anode is of graphite mixed with copper to increase its inertness. Cathode is usually of steel. As HF decreases in the electrolyte, more of it is added to prevent increase in resistance of the cell

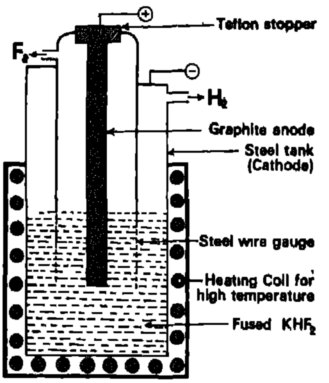


Fig. 10 2 Commercial preparation of fluorine.

Commercially fluorine is obtained by electrolyzing a 90% solution of KHF_2 in anhydrous HF The electrolysis is carried out in a steel tank using a copper mixed graphite anode and copper or steel cathode. A steel wire gauze is used as a gas barrier (Fig. 10 2). The anode, cathode and the barrier are insulated from one another with polytetrafluoro-ethylene $(C_2F_4)_n$ The fluorine obtained is compressed and stored in steel cylinders.

Properties . Fluorine is a pale greenish yellow gas It has a pungent odour which is more due to HF formed on the odour-sensitive surface inside the nose

Fluorine is the most reactive of all elements. It directly combines with all elements (except N_2 and O_2) including the higher noble gases, Kr and Xe

$H_2 + F_2 \rightarrow 2HF$ Explosive reaction (Even in total darkness and at low temperatures)

$S + 3F_2 \rightarrow SF_6$

Fluorine displaces all the other halogens from their ionic halides

$2NaX + F_2 \rightarrow 2NaF + X_2$; $(X = Cl, Br \text{ or } I)$

Fluorine is a powerful oxidizing agent It oxidizes water to ozonized oxygen.

Fluorine vigorously attacks hydrocarbons

$CH_4 + 2F_2 \rightarrow C + 4HF$.

However, by diluting fluorine with nitrogen, and in presence of copper fluoride as catalyst, a variety of products like CHF_3, CH_2F_2, CH_3F, CF_4, C_2F_6, and C_3F_8 can be obtained from the hydrocarbons. Mixed chloro-fluoro compounds have also been prepared by suitable methods. The hydrocarbons in which hydrogen atoms are replaced by fluorine atoms, are called *fluorocarbons*. The fluorocarbons are industrially important because of their extreme inertness. They are used as refrigerants, solvents, material for plastic preparation, lubricant, etc.

Reactivity The extraordinary reactivity of fluorine is due to the following reasons ·

(i) The dissociation energy of the F—F bond is the least.

	Fluorine	*Chlorine*	*Bromine*	*Iodine*
Bond dissociation energies (kJ/mol)	158	242	193	151

As a consequence, reactions with fluorine involve very small activation energies and can proceed at ordinary temperatures.

(ii) Fluorine atoms have the smallest size. This makes covalent bonds of fluorine atoms with other atoms relatively stronger and more exothermic. Fluorine can bring into operation the higher oxidation states of other elements

(iii) Fluorine has the highest electronegativity and therefore the tendency for forming ionic compounds is also highest in it. It can oxidize most of the other elements, even some of the inert gases. It can substitute for other elements in compounds.

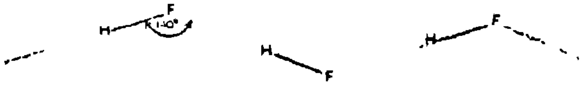
(iv) Stability and relative inertness of fluorocarbons and covalent fluorides like SiF_6, is due to non-availability of *d*-orbitals in the valency shell of fluorine atoms.

10.5 HYDROGEN FLUORIDE

It can be prepared by heating calcium fluoride with concentrated sulphuric acid

$$CaF_2 + H_2SO_4 \rightarrow CaSO_4 + 2HF$$

It is a colourless low boiling (b p. = 293K) liquid. At room temperature it exists as molecular aggregates due to hydrogen bonding. The H-F bond is very strong. So a solution of HF in water behaves as a weak acid It attacks many metals forming fluorides.



Hydrogen bonding in HF

Moist HF and its aqueous solution attack glass.

$$SiO_2 + 4HF \rightarrow SiF_4 + 2H_2O$$

$$SiF_4 + 2HF \rightarrow H_2SiF_6 \quad \text{(soluble in water)}$$

For this reason hydrofluoric acid solutions are kept in wax-coated glass bottles or plastic containers

Unlike the other hydrogen halides, HF gives acidic salts like KHF_2.

10.6 INTERHALOGEN COMPOUNDS

The halogens combine among themselves to give interhalogen compounds of the type AX, AX_3, AX_5 and AX_7. They can be prepared by the direct combination of the corresponding halogens under suitable conditions

Interhalogen compounds are more reactive than the elemental halogens (except in case of fluorine), because in halogens the heteroatomic bonds are weaker than the homoatomic bonds.

10.7 POLYHALIDES

Halide ions associate with molecules of halogens or interhalogen compounds to form polyhalide ions

$$I^- + I_2 \rightleftharpoons I_3^-$$
$$Cl^- + ICl \rightleftharpoons ICl_2^-$$

Fluorine does not form polyhalides because of the absence of *d*-orbitals in the valency shell of its atom.

10.8 BLEACHING POWDER

Bleaching powder ($CaOCl_2$) is obtained by passing dry chlorine over dry slaked lime at a temperature of 303-311K

$$Ca(OH)_2 + Cl_2 \rightarrow CaCl(OCl) + H_2O$$

When treated with dilute acids it liberates the whole of its chlorine.

$$CaCl(OCl) + 2H^+ \rightarrow Ca^{2+} + H_2O + Cl_2$$

Even CO_2 expels chlorine from bleaching powder suspended in water.

$$CaCl(OCl) + (H_2O + CO_2) \rightarrow CaCO_3 + H_2O + Cl_2$$

Chlorine obtained from a sample of bleaching powder on treating it with a dilute acid is called *available chlorine* for the sample.

Bleaching powder is an important ready source of chlorine It is used as a disinfectant, an oxidizing agent, and strong bleaching agent for cotton and jute.

10.9 SODIUM HYPOCHLORITE, NaOCl

This important bleaching agent for cotton cloth is obtained by the electrolytic oxidation of a stream of brine. The electrolysis is carried out in the cold and when the anode and the cathode are so close together that the products formed at the electrodes can react.

Brine contains water, Na^+ ions and Cl^- ions Electrode reactions can be written as

At cathode $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

At anode $2Cl^- \rightarrow Cl_2 + 2e^-$

$$2OH^- + Cl_2 \rightarrow Cl^- + OCl^- + H_2O$$

The solution coming out from the electrolytic cell contains Na^+, Cl^- and OCl^- ions From this NaOCl is separated by fractional crystallization.

10.10 ASTATINE

This halogen element was obtained artificially by bombarding bismuth with α-particles. Because of very small availability of the element, a detailed study of its properties has not been carried out. It is radioactive, and resembles iodine in its properties.

EXERCISES

10.1 Which of the halogens (excluding astatine) provide example of : (i) the weakest acid, HX, (ii) the largest atom, (iii) the smallest ionization energy, (iv) the strongest reductant, and (v) the best hydrogen bond former ?

10.2 How does HF differ from the other hydrogen halides ? Write chemical equations to show how bromide and iodide ions present in dilute solution may be estimated ?

10.3 Why is fluorine more reactive than the other halogens ?

10.4 Arrange the halogen hydrides in an increasing order of : (i) dipole moments, (ii) bond lengths, (iii) per cent ionic character, (iv) reducing power, and (v) thermal stability.

10.5 Why do we employ special methods for preparing HBr and HI ?

10.6 How do you explain the higher oxidation states shown by Cl, Br and I ?

10.7 How is it that HF is the least volatile and HCl the most volatile amongst hydrogen halides ?

10.8 Why do the halogens exhibit colours ?

10.9 Write an account of the positive oxidation states shown by the halogens

10.10 Why was the isolation of fluorine difficult ?

10.11 Why are the halogens strong oxidants ?

10.12 How is it that hydrogen halides in solution act as acids ? Why is it that HF is a weak acid while the other hydrohalo acids are strong ?

10.13 What are fluorocarbons ? What are their uses ?

10.14 What are the chemical changes involved in etching of glass with hydrofluoric acid ?

10.15 How is bleaching powder prepared ? What are its uses ?

10.16 Arrange the hydrogen halides in an order of increasing reducing power and thermal stability

10.17 The brown colour of an acidified dilute solution of iodine in aqueous potassium iodide is intensified by the addition of a nitrite but is discharged by the addition of a sulphite, comment (*Hint* Nitrites oxidize iodide ions to iodine; sulphites get oxidized to sulphates by iodine)

UNIT 11

Nuclear Chemistry

The change of nucleus of an atom of an element to form the nucleus of an atom of some other element can be regarded as a change of one substance into another As such, a nuclear change is of interest to chemists The branch of chemistry dealing with nuclear changes is called *nuclear chemistry*. Interest in nuclear chemistry has very much increased as nuclear changes provide a method for obtaining the much needed energy to make our lives comfortable There are several peaceful uses of nuclear changes in medicine, agriculture, archaeology and in many other fields A common factor in nuclear changes is the emission of certain rays from some substances. These rays were regarded in earlier observations as radiations, and the emission of these radiations was called *radioactivity* of the substances. These substances, in their turn, were called *radioactive*

11.1 THE DISCOVERY OF RADIOACTIVITY

In the year 1896 it was accidently discovered that crystals of potassium uranylsulphate left over a wrapped photographic plate showed some shadow marks on the plate after its development. This phenomenon could be repeated in total darkness. It was, therefore, inferred that potassium uranylsulphate crystals emitted some photographically active rays These rays were traced to the element uranium and on further investigation it was found that thorium compounds also emitted similar rays. The capacity of some elements to emit rays in this way was called radioactive power and the phenomenon was given the name radioactivity. Once discovered, radioactivity became a popular subject for scientific research. Now we have not only the naturally occurring radioactive elements but several man made radioactive elements also. If a substance emits radiations by itself, it is said to possess *natural radioactivity*. However, if a substance is not radioactive by itself; but begins to show new radioactivity under exposure to rays from a naturally radioactive substance, such a phenomenon is called *induced* or *artificial radioactivity*. We shall meet with examples of both kinds in this Unit

11.2 NATURE OF RADIATIONS FROM RADIOACTIVE SUBSTANCES

If the radiations from various radioactive substances are passed between the two poles of a strong electrostatic field (at right angles to the direction of field), three different types of behaviour are observed (Fig. 11.1).

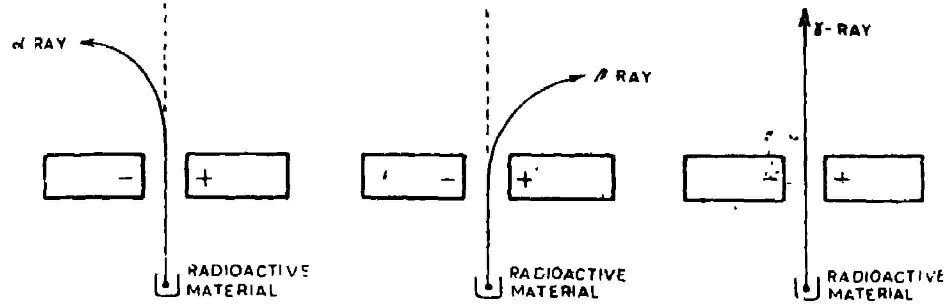


Fig. 11.1 Behaviour of α, β and γ emission subjected to an electric field

Some of the rays bend away from their initial path, while the rest remain undeflected In the first group of rays (which bend from their initial path) are of two types . (i) those which bend only a little and in one direction, and (ii) those which bend heavily and in just the opposite direction The lightly bending rays were called α-rays (alpha rays) Such rays were found to be coming out of uranium However, thorium was found to emit the rays bending heavily in the direction opposite to that of rays emitted in case of uranium. These were called the β-rays (beta rays). The non-bending third type of rays were called γ-rays (gamma rays).

Further investigations have shown that the α-rays consist of helium atoms which have lost their electrons. Thus, each α-ray particle has a mass of about 4 atomic mass units and a positive charge of two electronic units This information is shown by the symbols $_2^4\alpha$ or $_2^4\text{He}$ used for α-ray particles and helium nuclei. β-rays are found to consist of negatively charged particles which resemble electrons and are, in fact, electrons. A β-particle has a negligible mass and a negative charge of one electron unit It is given the symbol $_{-1}^{0}\beta$ or $_{-1}^{0}e$ The γ-rays are found to be similar to hard X-rays and are electromagnetic radiations of very short wavelength of the order of 0.1 nm or 1Å They are *massless* and *chargeless* The smaller deflection of α-rays is due to their heavy mass and large momentum Heavy deflection of β-rays is due to their momentum being relatively much smaller. Absence of charge and mass in γ-rays is responsible for no deflection being observed in their case.

α-rays can penetrate 0.002 cm, β-rays can penetrate up to 0.2 cm, and γ-rays can penetrate as much as 100 cm of thick aluminium sheet respectively.

11.3 CHANGES IN NUCLEI DURING RADIOACTIVITY

During nuclear changes, α- and β-particles are thrown out from the nuclei of radioactive elements An α-particle can be regarded as a combination of 2 neutrons and 2 protons to make up for its mass number, 4, and its charge of two positive electronic units Obviously, after emission of an α-particle from an atomic nucleus, the new nucleus formed must have a mass number which is smaller than that of the original nucleus by 4 units The positive charge or the proton number for the residual nucleus must be less by 2 units than that of the original nucleus This will also mean that the *atomic number* for the new nucleus will be less by 2 compared to the atomic number of the original nucleus Another thing will be an immediate adjustment in the number of electrons in the energy shells round the nucleus so that finally a neutral atom is obtained for a new element

In α-particle emission, atomic number of the new or *daughter* element is smaller by 2 *units and its mass number is smaller by 4 units than the original or parent element*

Any decrease in mass, howsoever small, will be converted to energy in the form of γ-rays A chemist is concerned with the change in atomic number, as this means the formation of a new element Radioactivity is, therefore, also called *transmutation* of elements The daughter element whose atomic number is smaller by 2, will have a position in the Periodic Table two places to the left of the position of the parent element *A group displacement occurs as a result of the emission of an α-particle.* The new element will be an isotope of the element already present in this new position two groups behind the group of the parent element

Let us now consider the nature of change in a nucleus after it has emitted a β-particle When a nucleus emits a β-particle, one of the neutrons in the nucleus is converted into a proton. Since the mass number for a proton and a neutron are the same, emission of a β-particle will not cause any change in the mass number of the nucleus However, as the new nucleus will have one proton more, the atomic number for the new nucleus or of the daughter element corresponding to it will be more by 1 compared to the parent element The daughter element will occupy in the Periodic Table one position ahead of the parent element A group displacement and a transmutation of element accompany the emission of a β-particle An adjustment in energy of the new nucleus and in the number of extra-nuclear electrons completes the β-ray change.

Without going into any further discussion we can say that emission of γ-rays alone by any nucleus will not amount to any change in atomic number, group displacement or transmutation of element It will only mean lesser energy in the nucleus. γ-ray emissions are observed from nuclei which are left in an excited state by an earlier emission of α-or β-particles.

*Group Displacement Law** The new element formed as a result of emission of an α-particle from the nucleus of atom of a radioactive element occupies a position two groups to the left of that of the initial element and the new element formed by the emission of a β-particle from the nucleus of a radioactive element occupies a position one group to the right of that of the initial element in the Periodic Table

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*In some cases of artificial disintegration of elements, positrons, $_{+1}^{0}e$, are also emitted In such cases, the atomic number of a daughter element will be one less than that of a parent element

Example 11.1

After emitting some α-and some β-particles, we pass down the series from ${}^{238}_{92}U$ to ${}^{206}_{82}Pb$. How many α-and β-particles must have been lost in this series change ?

Solution

Transition ${}^{238}_{92}U \longrightarrow {}^{206}_{82}Pb$

Loss in mass number = 238 − 206 = 32

Decrease in atomic number − 92 − 82 = 10

Loss in mass number can be set for α-particle emissions. Since each particle accounts for a decrease of 4 units, number of α-particles corresponding to a decrease of 32 will be 8.

When 8 α-particles are lost by a nuclide, its atomic number should decrease by 16. Actual decrease observed is 10 To account for the difference of 6 in atomic numbers there should be a loss of 6 β-particles also Therefore

Number of α-particles lost = 8

Number of β-particles lost = 6

Example 11 2

Ra-226 is an α-emitter and Bi-210 is a β-emitter. In what groups will the daughter elements be and what shall be their atomic numbers ?

Solution

Radium has an atomic number of 88 and its place is in group IIA The daughter elements would have an atomic mass of 222 and an atomic number 86. According to the Periodic Table, this element is radon. It is present in the group 0 or amongst the noble gases. The daughter element from ${}^{210}_{83}Bi$ will be ${}^{210}_{84}Po$ which is one group ahead of bismuth. The change will be from group VA to group VIA

11.4 CHEMICAL EQUATIONS FOR NUCLEAR CHANGES

In nuclear changes, basically nuclei of atoms are involved. From one initial nucleus, one new nucleus is formed and any change in mass and charge numbers is adjusted by putting into the equation a requisite number of other involved particles. In radioactive changes, these other particles are the α- or the β-particle. By a convention, now universally adopted, we use for nuclei the same symbols as for the relevant atoms or elements However, we add the mass number and the charge number for a nuclear symbol on its left side. Thus ${}^{4}_{2}He$ stands for a nucleus of helium whose mass number is 4 and charge number or atomic number is 2. This nuclear species is also called the helium-4 species. The atomic number of the species follows from the name ${}^{238}_{92}U$ stands for the nucleus of uranium isotope, uranium-238, atomic number and nuclear charge number being 92.

Two examples of nuclear equations are :

(i) Uranium-238 ——→ Thorium-234 + α-particle

or $^{238}_{92}\text{U} \longrightarrow {}^{234}_{90}\text{Th} + {}^{4}_{2}\text{He}$

(ii) Thorium-234 —→ Protoactinium-234 + β-particle

or $^{234}_{90}\text{Th} \longrightarrow {}^{234}_{91}\text{Pa} + {}^{0}_{-1}\text{e}$

1.4-1 RADIOACTIVE DISINTEGRATION SERIES

Spontaneous disintegration of any nuclear species is a change leading from a less table substance to a more stable one. However, complete stability may not be eached in a single step The daughter element may still be radioactive and, thus, we an have a chain of disintegration steps. This chain continues till a final stable nuclear species is reached All the nuclei from the initial element to the final stable element constitute a series which is called a *disintegration series,* Since mass numbers change only when α-particles are emitted (and not when β-particles are emitted), the change is of 4 units at each step. The mass numbers of all elements in a series will fit into one of the formulae 4n, 4n+1, 4n+2, or 4n+3

Thus, there can be only four disintegration series 4n+1 series consists of man made elements and the other three series are of naturally occurring elements These series are

4n series : Thorium series from thorium-232 to lead-208 (value of n for thorium is 58 and for lead is 52)

4n+1 series : Neptunium series from neptunium-237 to bismuth-209 (value of n for neptunium is 59 and for bismuth is 52)

4n+2 series : Uranium series from uranium-238 to lead-206 (value of n for uranium is 59 and for lead is 51)

4n+3 series : Actinium series from uranium-235 to lead-207 (value of n for uranium is 58 and for lead is 51)

Before proceeding further, we may define two more terms used in nuclear chemistry. The first one is *nucleon.* It is the common name for particles constituting the nuclei, and can be used for neutrons and protons collectively Thus, we may say that the helium nucleus consists of four nucleons. The second term is the *nuclide.* A nuclide refers to a nucleus with specific atomic number and atomic mass. Thus, the alpha decay of uranium-238 nuclide leads to the formation of the thorium-234 nuclide

$$^{238}_{92}\text{U} \rightarrow {}^{234}_{90}\text{Th} + {}^{4}_{2}\text{He}$$

For nuclide of one element the term 'isotope' is frequently used.

11.5 ARTIFICIAL TRANSMUTATION OF ELEMENTS

We have seen up to now how naturally radioactive elements get transmuted or transformed into new elements. It has been found that radioactivity of an element is not changed in any way by a change in the chemical combination of the element or by changing the temperature or pressure on a substance. This shows that radioactivity is a property of atomic nuclei. These are not influenced in any way during chemical or physical changes. Thus, the nature of particles emitted, the rate at which they are emitted, or the energies with which they are emitted remain beyond man's control.

The scientists tried another approach. They planned to bombard atomic nuclei with particles, which were themselves of atomic or sub-atomic sizes and had high speeds. In the initial stages, experiments were conducted with α-particles available from naturally radioactive elements Blackett and Rutherford reported the reaction between nitrogen nuclei and α-particles obtained from radium.

$$^{14}_{7}N+{}^{4}_{2}He \longrightarrow {}^{17}_{8}O+{}^{1}_{1}H$$

The slow rate of this reaction indicated the great difficulty in reaching a positively charged atomic nucleus with the help of a positively charged α-particle projectile. Rutherford's experiment proved the feasibility of artificial transmutation of elements, but the means for absolute success were not then available

Another atomic bombardment experiment of great historic importance was of W. Bothe and H. Becker of Germany conducted in 1930. A new fast moving particle with great penetrating power was discovered in the bombardment of beryllium with α-particles. It was undeflected by magnetic field In 1932, James Chadwick of England showed that this chargeless particle had a mass almost equal to that of the proton. He called it *neutron*. Neutron was given the symbol $^{1}_{0}n$

$$^{9}_{4}Be+{}^{4}_{2}He \longrightarrow {}^{12}_{6}C+{}^{1}_{0}n$$

In the meantime, accelerating machines were constructed for accelerating the available sub-atomic particles like the α-particle and the proton so that they could be given momenta large enough to counteract the coulombic repulsions of atomic nuclei. The *cyclotron* was one such machine. More successful bombardments were achieved and several planned and unplanned transmutations of elements were carried out. The following equations illustrate a few of the experiments :

$^{39}_{19}K+{}^{1}_{1}H \longrightarrow {}^{36}_{18}Ar+{}^{4}_{2}He$ (p,α)

$^{23}_{11}Na+{}^{2}_{1}H \longrightarrow {}^{21}_{10}Ne+{}_{2}He$ (d,α) (d means deuterium)

$^{12}_{6}C+{}^{1}_{1}H \longrightarrow {}^{13}_{7}N+{}^{0}_{0}\gamma$ (p,γ)

$^{14}_{7}N+{}^{1}_{0}n \longrightarrow {}^{14}_{6}C+{}^{1}_{1}H$ (n,p)

The transmutation reactions are usually classified according to the nature of the bombarding particle and of the ejected particle (they are named in this very order). Historically important transmutation is the bombardment of aluminium by α-particles from polonium, carried out by Irene Curie and F. Joliot. Aluminium appeared to keep on emitting positrons even when bombardment with α-particles was stopped. It was the first observed case of *artificial* or *induced radioactivity*.

The following changes take place .

$$^{27}_{13}\mathrm{Al} + ^{4}_{2}\mathrm{He} \longrightarrow ^{30}_{15}\mathrm{P} + ^{1}_{0}\mathrm{n} \qquad (\alpha,\mathrm{n})$$

$$^{30}_{15}\mathrm{P} \longrightarrow ^{30}_{14}\mathrm{Si} + ^{0}_{+1}\mathrm{e}$$

The observed positron emission was from the product element, phosphorus, but it appeared as if the aluminium had been induced to become radioactive. Thus, what we speak of as induced radioactivity of aluminium is actually the radioactivity of $^{30}_{15}\mathrm{P}$

As a positively charged particle (proton or α-particle) approaches the atomic nucleus due to coulombic repulsion, potential energy of the system increases (Fig. 11.2) This happens up to a certain distance near the nucleus Once the particle gets near enough, a strong attraction comes into play. At this close distance, nucleons show extremely strong attraction irrespective of their charges.

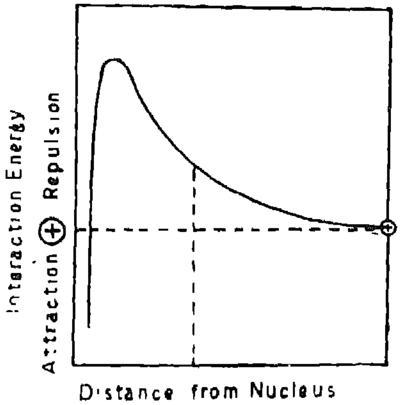

Fig 11 2 Potential energy diagram of an α-particle-atomic nucleus system

Particle energies are often stated in units of electron volts (eV). This is the energy gained by a particle of 1 electronic unit of charge when it moves in an electric field over a potential difference of 1 volt α-particles of natural radioactivity have energies of 5 to 8 million electron volts (MeV) per particle Accelerators can now produce particles with energies in the range of billion electron volts (or giga electron volt, GeV*).

Some important aspects such as induced radioactivity, stability of atomic nuclei, energy changes in nuclear transmutations, fission and fusion of nuclei, and uses of radioisotopes and radiation hazards are dealt with under Nuclear Physics in the *Physics Textbook*. Part II We shall now discuss some of the kinetic aspects of nuclear changes.

11.6 DISINTEGRATION RATES AND DISINTEGRATION CONSTANTS

In all radioactive disintegrations, the number of atoms disintegrating is proportional to the number of such atoms (nuclei) present. This is characteristic of first order reactions (Unit 5). The rate of decrease in the number of disintegrating atoms can be written as

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*1Gev = 1 giga electron volt = 10^9 electron volt = 1 billion electron volts

$$-\frac{dN}{dt} \propto N$$

$$\text{or} \quad -\frac{dN}{dt} = \lambda N \qquad \ldots (11.1)$$

where N is the number of radioactive nuclei present at any instant. The proportionality constant λ in this case is called *disintegration* or *decay constant* It has a characteristic value for a given radioactive element. Eq 11 1 may be rearranged as

$$\frac{dN}{N} = -\lambda\, dt \qquad \ldots (11.2)$$

On integration, we get ·

$$\ln \frac{N}{No} = -\lambda t$$

$$\text{or} \quad N = Noe^{-\lambda t}$$

$$\text{Also,} \quad 2.303 \log \frac{N}{No} = -\lambda t$$

$$\text{or} \quad \log \frac{No}{N} = \frac{\lambda t}{2.303} \qquad \ldots (11.3)$$

No is the number of radioactive atoms present at $t = 0$. It follows from Eq 11.3 that radioactive disintegration is an exponential decay process.

11.6-1 HALF-LIFE PERIOD

Like other first order reactions we can also have half-life of radioactive decays Half-life period is a characteristic property of a radioactive species. It is the time required for the disintegration of one-half of the atoms of radioactive species initially present. Different radioactive substances have different half-life periods. For example, half-life period of $^{238}_{92}U$ is 4.51×10^{9} years; of $^{226}_{88}Ra$ is 1590 years; and that of $^{216}_{84}Po$ is 1.5×10^{-4} seconds.

The condition for half-life is that $N = \frac{1}{2} No$. Substituting this value in Eq 11.3. we get .

$$\log 2 = \frac{\lambda t_{\frac{1}{2}}}{2.303}$$

$$\text{or} \quad t_{\frac{1}{2}} = \frac{2.303 \log 2}{\lambda}$$

$$= \frac{0.693}{\lambda}$$

Here, $t_{\frac{1}{2}}$ represents the half-life period. Thus, if the disintegration constant (λ) is known, the half-life period ($t_{\frac{1}{2}}$) of the radio-element can be evaluated and vice versa The half-life period, which is inversely proportional to the disintegration constant, is thus independent of the amount of radio-element initially present. The amount of decay of any radio-element is independent of temperature, pressure, and other physical conditions. It is governed solely by the lengths of time and its disintegration constant.

A typical radioactive disintegration curve is shown in Fig. 11.3 in which the fraction of

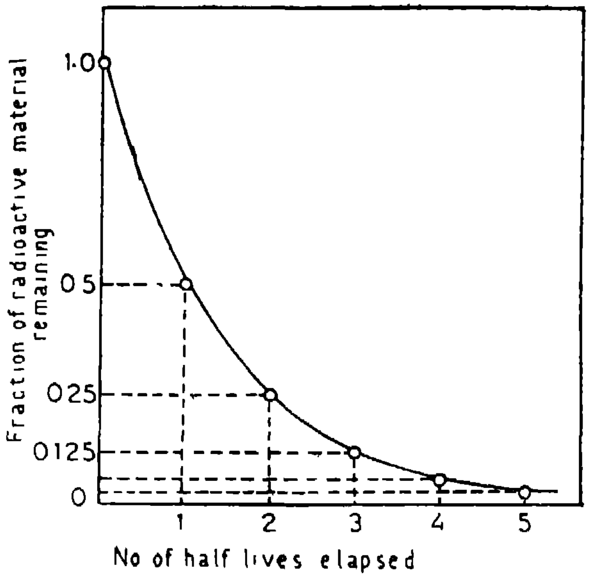

Fig 11 3 Schematic diagram of decay of a radioactive element

the amount of radioactive substance is plotted against time. The knowledge of the principles of half-lives have been extremely valuable in determination of geological times

11.7 CARBON DATING

Half-life principle forms the basis of the carbon dating method. ${}^{14}_{6}C$ is produced in the upper atmosphere by cosmic ray-bombardment of nitrogen and gradually reaches our atmosphere

$$ {}^{14}_{7}N + {}^{1}_{0}n \longrightarrow {}^{14}_{6}C + {}^{1}_{1}H $$

C-14 decays according to the equation .

$$ {}^{14}C \longrightarrow {}^{14}_{7}N + {}^{0}_{-1}e $$

Since number of cosmic rays impinging on the earth is relatively constant, the production and disintegration rates of C-14 are constant Under the circumstance, an equilibrium is maintained not only between the rates of formation and disintegration of C-14 but also between C-14 and C-12 content of atmospheric CO_2 This means that the concentration of C-14 in the atmosphere has been constant for several millions of years This amount of C-14 is extremely small. However, its radioactive properties make its detection and estimation easily possible Carbon-14 dioxide is in turn incorporated into living plants by the process of photosynthesis. These plants are eaten up by the animals and, thus, carbon-14 is incorporated in their systems Any living material has the equilibrium percentage of carbon-14 in it so long as it is alive. As soon as it dies, it ceases to incorporate any more carbon-14. Carbon-14 already present in it begins to decay and its carbon-14 content gradually drops off. We know that half-life period of carbon-14 is 5,760 years. In 5,760 years, its concentration is cut to half and after 11,520 years only 25% of the initial concentration remains. This process of decreasing concentration continues. If we know the equilibrium concentration of C-14 and its concentration in a dead piece of wood at a particular time, the material can be dated. We can calculate the age of the material using the half-life constant for C-14. It is very important to note that it is assumed that the normal concentration of carbon-14 several thousands years ago was the same as it is today

Suppose, we have a piece of charcoal from a campfire at an archaeological find and we wish to date it. For simplicity let us assume the equilibrium concentration of C-14 is 1%. Now, radioactivity (which depends on its C-14 concentration) of charcoal is measured and let us suppose it contains 0.125% of the C-14. Of it 0.5% would have remained after the first half-life, 0.25% after the second half-life, and 0.125% after the third half-life Thus, three half-lives must have elapsed since the wood was cut for the fire. Thus, the age of the find is 3 × 5,760 years or 17,280 years. This method is of immense use in geological and archaeological fields One can understand the importance of the method by the fact that Willard Libby (University of California) was awarded Nobel Prize for work in radiocarbon dating

This method of dating can be effectively used up to 60,000 years There are also other isotopic elements which may be used to establish ages significantly greater than 50,000 years, but such description is beyond the scope of the present text.

Example 11.3

A wood piece from an archaeological find has only 25% as much C-14 activity as a fresh piece of wood Calculate the age of the piece of wood $t_{\frac{1}{2}}$ for C-14 is 5,760 years.

Solution

$$No = 100\%, \quad N = 25\% \text{ of } No = 25\%$$

$$t_{\frac{1}{2}} = \frac{0.692}{\lambda} = 5{,}760 \text{ years}$$

$$\therefore \lambda = \frac{0.692}{5760} = 1.2 \times 10^{-4} \text{ years}^{-1}$$

$$\lambda t = 2.303 \log \frac{No}{N} \text{ (vide Eq. 11.3)}$$

$$\therefore t = \frac{2.303}{1.2 \times 10^{-4}} \log 4 = \frac{2.303 \times 0.602}{1.2} \times 10^4 = 11{,}520 \text{ years}$$

11.8 MASS ENERGY CONVERSIONS

In transmutation experiments one comes across situations in which masses disappear when huge amounts of energy are generated. For mass-energy conversions the following equation given by Einstein and known as ***Einstein's mass-energy relationship*** holds:

$$E = mc^2 \qquad \text{.. ......(11.4)}$$

In this equation, the energy, *E*, will be in joules if the mass, *m*, is in kilograms and velocity of light, *c*, is in metres per second. Energy is directly proportional to mass disappearing. Because of a very large value of velocity of light, disappearance of extremely small masses will yield extremely large values of energy. It is the ***quantity*** of mass which goes into above relationship and not its ***quality*** or kind.

Example 11.4

Calculate the loss in mass accompanying combustion of one mole of CH_4 which yields 890kJ of energy.

Solution

$$\Delta E = -890 \text{ kJ}, \quad c = 3\times10^8 \text{ m/sec}$$

since $\Delta E = \Delta mc^2$

$$\Delta m = \frac{\Delta E}{c^2} = -\frac{890\times10^3 \text{J}}{(3\times10^8)^2 \text{ m}^2/\text{sec}^2}$$

$$= -9.89\times10^{-12} \frac{\text{J}}{\text{m}^2/\text{sec}^2}$$

since 1 joule = 1 kg m^2/sec^2

$$\Delta m = -9.89\times10^{-12} \frac{\text{kg m}^2/\text{sec}^2}{\text{m}^2/\text{sec}^2}$$

$$= -9.89\times10^{-12} \text{ kg}$$

Thus, a change in mass accompanying a chemical change is quite outside the limits of experimental measurements

Example 11.5

An α-particle has a mass of 4.00150 amu. It can be treated as made from the two neutrons and two protons The neutron has a mass of 1.00867 amu and a proton of 1.00728 amu If 6.02×10^{23} amu equal 1 gram of mass, calculate the energy released during formation of a mole of α-particles

Solution

Mass of 2 neutrons = 2×1.00867 = 2.01734 amu
Mass of 2 protons = 2×1.00728 = 2.01456 amu

Total mass = 4.03190 amu
Mass of α-particle = 4.00150 amu
Therefore,
Loss in mass for one particle = 0.03040 amu

Hence, 0.0304, amu $= \frac{1.0000}{6.02\times10^{23}}\times0.0304$ g

Loss in mass for 1 mole of α-particles $= \frac{1}{6.02\times10^{23}} \times 0.0304 \times 6.02\times10^{23}$ g

$= 0.0304$ g $= 3.04\times10^{-5}$kg

Energy equivalent to $3.04\times10^{-5}\text{kg} = 3.04\times10^{-5}\times9.0\times10^{16}\ \text{J} = 2.74\times10^{12}\ \text{J}$
Loss of such a large amount of energy is responsible for the stability of α-particles.

11.9 SYNTHETIC ELEMENTS

Uranium was the limit of elements occurring in nature. It was natural to enquire if there could be elements with atomic numbers more than 92. When it was found that by bombarding atomic nuclei with neutrons and accelerated protons and α-particles lower elements could be transmuted to neighbouring ones and that the elements missing in the Periodic Table at atomic numbers 43 (Technetium), 61 (Promethium) and 87 (Francium) could be synthesized by bombarding atomic nuclei with fast sub-atomic particles, attempts were made to produce elements beyond uranium by a similar method. There was quite a bit of success. Gradually, heavier ions came to be used as bombarding particles. Now the Periodic Table shows elements up to atomic number 105. The elements coming after uranium are called *transuranic* or *transuranium elements*. They are all synthetic in nature and are man made. They are radioactive and most of them have short half-lives. The following nuclear equations depict the formation of some of the new elements.

$$^{238}_{92}\text{U} + {}^{1}_{0}\text{n} \longrightarrow {}^{239}_{92}\text{U} \longrightarrow \underset{\text{Neptunium}}{^{239}_{93}\text{Np}} + {}^{0}_{-1}\text{e}$$

$$^{239}_{93}\text{Np} \longrightarrow \underset{\text{Plutonium}}{^{239}_{94}\text{Pu}} + {}^{0}_{-1}\text{e}$$

$$^{240}_{94}\text{Pu} + {}^{1}_{1}\text{H} \longrightarrow \underset{\text{Americium}}{^{241}_{95}\text{Am}}$$

$$^{239}_{94}\text{Pu} + {}^{4}_{2}\text{He} \longrightarrow \underset{\text{Americium}}{^{241}_{95}\text{Am}} + {}^{1}_{1}\text{H} + {}^{1}_{0}\text{n}$$

$$^{241}_{95}\text{Am} + {}^{4}_{2}\text{He} \longrightarrow \underset{\text{Berkelium}}{^{243}_{97}\text{Bk}} + 2{}^{1}_{0}\text{n}$$

Elements up to atomic number 103 have been named. The element with atomic number 104 is being currently called Kurchatovium* (Ku) and that with 105 Hahnium (Ha).

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*Name is not yet final. It is also called Rutherfordium.

EXERCISES

11.1 State the numbers of neutrons, protons and nucleons in the following nuclides·

(i) Carbon – 14, (ii) $^{24}_{11}$Na, (iii) Uranium-238, (iv) $^{40}_{18}$Ar

11.2 Write nuclear equations for the following transformations .

(i) Thorium – 232 decays to radium – 228

(ii) $^{241}_{94}$Pu emits a β-particle

(iii) $^{88}_{39}$Y emits a positron (β+)

11.3 Complete the following equations .

(i) $^{27}_{13}\text{Al} + ^{4}_{2}\text{He} \rightarrow \cdot\cdot \;+ ^{1}_{1}\text{H}$

(ii) $^{27}_{13}\text{Al} + \cdot\cdot \rightarrow ^{30}_{15}\text{P} + ^{1}_{0}\text{n}$

(iii) $\ldots \rightarrow ^{24}_{12}\text{Mg} + ^{0}_{-1}\text{e}$

(iv) $^{235}_{92}\text{U} + ^{1}_{0}\text{n} \rightarrow \cdot\cdot + ^{140}_{56}\text{Ba} + 2\,^{1}_{0}\text{n}$

11.4 Write equations for the following processes .

(i) $^{14}_{7}$N (n,p), (ii) $^{15}_{7}$N (p,α)

11.5 Calculate the α-and-β-particles emitted in the thorium series in reaching lead-208 from thorium-232

11.6 (a) One microgram of Na-24 is injected into the blood of a patient. How long will it take the radioactivity to fall to 10% of initial value ? ($t_{\frac{1}{2}}$ for Na-24 is 14.8 hours)

(b) Half life of tritium (hydrogen-3) is 12.3 years. If we seal 20×10^{-6} kg of it in a tube today, how much of it will remain in the tube after 6.15, 12 3 and 24 6 years ?

11.7 100 mg of Co-60 is stocked in a laboratory as a γ-ray source. It has a half-life of 5.26 years Calculate the percentage decrease in its activity after one year

11.8 Calculate the age in the following cases :

(i) A piece of hair in which C-14 activity is 60% of the activity found today ($t_{\frac{1}{2}} = 5{,}760$ years).

(ii) A vegetarian beverage whose tritium content is only 5% of level in living plants ($t_{\frac{1}{2}} = 12\ 3$ years).

(iii) A uranium rock has uranium-238 and lead-206 in a mass ratio of 1.50 to 1.00. ($\lambda = 1\ 52 \times 10^{-10}$ year^{-1})

11.9 The disintegration rate of a radioactive element changes from an initial value of 3112 disintegrations per minute to 980 disintegrations per minute in 42 days. Calculate the disintegration constant and half-life period for this element.

11.10 Rutherford observed transmutation of an element on bombarding nitrogen with α-particles but not when the gold plate was bombarded with the same particles. Suggest a reason.

11.11 For transmutation experiments α-particles and protons are accelerated but this is not so for neutrons Explain.

11.12 Suggest if the following radioactive elements will or will not be accumulated in our body ? If accumulation is indicated suggest the possible location also.
Strontium-90, iodine-131, krypton-87, iron-56.

11.13 Calculate the number of C-14 atoms in the body of a man weighing 70 kg, if percentage of carbon in human body is taken as 18 and 1 molecule in every 10^{12} molecules of CO_2 in air contains carbon-14 atom.

UNIT 12

The Noble Gases

The gaseous elements helium, neon, argon, krypton, xenon and radon constitute the zero group of periodic table. Because of their low abundance on the earth, they have been called *rare gases*, and due to their chemical inertness, they have been called inert or noble gases. With the discovery that some of them can form compounds under suitable conditions, we no longer refer to them as inert gases All of them, except helium, have the closed shell, np^6, configurations Helium has the ls^2 configuration. The electronic configuration accounts for their high degree of chemical inertness in ordinary chemical reactions

12.1 OCCURRENCE

All the noble gases, except radon, are present in atmosphere The relative percentages of the noble gases in dry air are given in the following table

TABLE 12.1

Relative Abundance of Zero Group Elements in Dry Air

Element	*Percentage*
Helium (He)	5.2×10^{-4}
Neon (Ne)	1.8×10^{-3}
Argon (Ar)	9.3×10^{-1}
Krypton (Kr)	1.1×10^{-4}
Xenon (Xe)	8.7×10^{-6}
Radon (Rn)	—

In addition helium is present up to 10 per cent in natural gas (the gas emanating from certain petroleum bearing regions). It also results from the decay of certain radioactive elements and is found in some uranium minerals. Radon is produced in the radioactive decay of radium.

12.2 DISCOVERY OF THE NOBLE GASES

In 1785, Cavendish observed that when air was sparked with an excess of oxygen and the unreacted oxygen removed, a small residual gas was left behind which would not combine with oxygen or any other element This discovery was not taken serious note of till 1895. In that year, Rayleigh found that nitrogen obtained from atmosphere showed a density of 1.2574 while nitrogen from chemical sources has a density of 1.2505 only By passing nitrogen obtained from air repeatedly over heated magnesium, Ramsay obtained small amount of a residual gas Spectroscopic examination of this gas showed that it was a new gas, different from nitrogen. From its inertness it was named argon (meaning inert).

Helium was first detected spectroscopically by Lochyer in sun's atmosphere It was later identified in the gas evolved from certain radioactive minerals

With the discovery that atmospheric air is the chief source for noble gases, a thorough fractionation of liquid air was carried out This resulted in the discovery of neon, krypton and xenon.

Radon was identified as a disintegration product of radium.

12.3 PROPERTIES

The outer electronic configuration and the general trends in properties of the noble gases are summarised in Table 12.2.

TABLE 12.2

Electronic Configuration and General Trends in Properties of Noble Gases

Element	Atomic number	Outer electronic configuration	ΔH_{fus} (kJ mol⁻¹)	ΔH_{vap} (kJ mol⁻¹)	Ionization energy (kJ mol⁻¹)	b. p (K)	m. p. (K)	vander Waals' radius (Å)
He	2	$1s^2$	0.02	0.084	2372	—	—	—
Ne	10	$2s^2 2p^6$	0.33	1.77	2081	27	24	1.31
Ar	18	$3s^2 3p^6$	1.18	6.5	1520	87	84	1.74
Kr	36	$4s^2 4p^6$	1.64	9.0	1350	121	116	1.89
Xe	54	$5s^2 5p^6$	2.3	12.6	1170	166	161	2.1
Rn	86	$6s^2 6p^6$	2.9	16.4	1040	211	202	2.15

All of them are monoatomic, colourless, odourless gases They are sparingly soluble in water. They have low melting and boiling points. The inter-atomic forces in the noble gases are very weak. The first member of the group, helium shows some abnormal properties. Thus if helium is cooled to 2.2K at 1 atmosphere, liquid helium called helium-I changes into helium-II which has abnormal physical properties.

The noble gases other than radon can be obtained by the fractionation of liquid air

12.4 USES

The noble gases are widely used to provide an inert atmosphere in welding and cutting, inside electric bulbs and in metallurgical operations. As liquids they are used for providing very low temperatures

Helium because of its lightness and non-inflammability is used to fill air ships and observation balloons. Helium-oxygen mixture is used by deep sea in preference to nitrogen-oxygen mixtures. It is much less soluble in blood than N_2. This prevents the bends. "Bends" is the pain caused by formation of nitrogen bubbles in blood veins when a diver rises to the surface

Neon, argon and xenon are used to fill coloured discharge tubes for optical decorations and advertising

Radon is an active intermediate in treating cancer with radium

12.5 COMPOUNDS OF THE NOBLE GASES

Because of their high ionization energies and the closed shell electronic configurations the noble gases do not form compounds like other elements

It was noticed that when oxygen reacted with platinum hexafluoride, hexafluro platinate $O_2^+[PtF_6^-]$ was formed. Because xenon and oxygen have similar first ionization energies, it was thought that xenon could also give a similar product. This prediction was verified by Bartlett in 1962 and he prepared the compound $Xe^+PtF_6^-$. This discovery stimulated the search for other noble gas compounds

Soon many compounds of xenon with fluorine were prepared.

$$Xe + 3F_2 \xrightarrow{573K} XeF_6$$

$$Xe + 2F_2 \xrightarrow{673K} XeF_4$$

$$Xe + F_2 \xrightarrow{\text{light from mercury arc}} XeF_2$$

The bonding in these compounds is covalent. It involves electron promotion from the *p* to the unoccupied *d* levels of the xenon atom. The highly electronegative fluorine is able to induce this type of promotion of electrons in xenon atoms.

While xenon difluoride is a linear molecule, the tetrafluoride is a square planar molecule (Fig. 12.1).

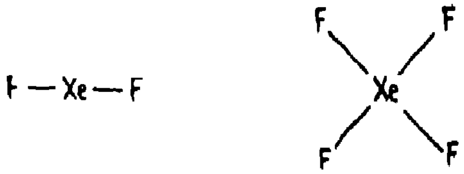

Fig 12.1 Structures of XeF_2 and XeF_4 molecules

The noble gases argon, krypton and xenon when compressed with water give hydrates containing 6 molecules of water for each noble gas atom. It is regarded that in such compounds the noble gas atoms are trapped in a net work of water molecules. The water molecules are held together by hydrogen bonding. Such compounds are termed '*enclosure' compounds* or '*clathrate*' compounds.

EXERCISES

12.1 Why are the noble gases in general chemically inert ?

12.2 The outer electron configurations of the noble gases provide a key to chemical bonding. Discuss.

12.3 Give an account of the isolation of the noble gases.

12.4 What are the chief uses of noble gases ?

12.5 How do you account for the formation of xenon fluorides ? Give the molecular structures of XeF_2 and XeF_4.

12.6 How do you justify the inclusion of the noble gases in the zero group of the periodic table ?

12.7 Why the name 'inert gases' has now been given up for the zero group elements ?

12.8 Why do xenon and bromine, and argon and fluorine not form compounds like xenon fluorides.

(Hint Electronegativity differences and promotion possibilities of electrons not helpful)

UNIT 13

Metallurgical Operations

The elements in the periodic table broadly fall into two major types, metals and non-metals. The first type is characterized by low values for their ionization energies, electron affinities and electronegativities as compared to the much higher values shown by the elements of the second type. The occurrence and recovery of metals largely depends on their properties

13.1 OCCURRENCE OF METALS

The metals differ very widely in their reactivities. The few unreactive ones may occur in nature in a free state or native form. Thus, platinum and gold occur free in nature. Silver occurs native as well as in the form of compounds The reactive metals, by their very nature, cannot occur in free state. Solid compounds of metals occurring in nature are termed *minerals*. Thus NaCl, KCl, $CaCO_3$, $MgCO_3$, ZnS, HgS, Cu_2S, Fe_2S_3, etc. which occur in nature are all minerals.

The minerals form the chief source of metals. However, it would be possible to obtain a metal economically only from some minerals and not others Such minerals which are used for commercial preparation of a metal, are called its *ores*. Both bauxite $Al_2O_3 . 2H_2O$ and clay, $Al_2O_3 . 2SiO_2 . 2H_2O$ contain minerals of aluminium However, bauxite is principally used in the commercial production of aluminium. So bauxite, and generally not clay, is referred to as an ore of aluminium. Table 13.1 gives the minerals of some metals. The minerals used as ores are marked with an asterisk (*). Metals can be extracted profitably from ores.

TABLE—13.1**

Metals and Their Important Minerals

Metal	*Minerals with their Chemical Formulas*
Sodium	Rock Salt—NaCl* Chile Salt petre—$NaNO_3$ Borax—$Na_2B_4O_7$

**The table is not intended for memorization.

Potassium	Sylvine—KCl^* Carnallite—$KCl.MgCl_2.6H_2O$ Felspar—$K_2O.Al_2O_3.6SiO_2$
Calcium	Limestone—$CaCO_3^*$ Dolomite—$CaCO_3.MgCO_3$ Gypsum—$CaSO_4.2H_2O$
Copper	Malachite—$CuCO_3.Cu(OH)_2^*$ Copper glance—Cu_2S^* Copper pyrites—$Cu_2S.Fe_2S_3^*$
Magnesium	Asbestos—$CaSiO_3.3MgSiO_3$ Magnesite—$MgCO_3^*$ Dolomite—$CaCO_3.MgCO_3^*$ Carnallite—$KCl.MgCl_2.6H_2O^*$
Silver	Silver glance—Ag_2S^* Horn silver—$AgCl^*$ Native silver*
Gold	*Native gold**
Zinc	Zinc blende—ZnS^* Zincite—ZnO^* Calamine—$ZnCO_3^*$
Mercury	Cinnabar—HgS^*
Aluminium	Bauxite—$Al_2O_3.2H_2O^*$ Cryolite—$3NaF.AlF_3$
Tin	Cassiterite or Tin stone—SnO_2^*
Antimony	Stibnite—$Sb_2S_3^*$
Lead	Galena—PbS^*
Bismuth	Bismuth glance—$Bi_2S_3^*$
Chromium	Chromite—$FeO.Cr_2O_3^*$
Manganese	Pyrolusite—MnO_2^*

Iron	Haematite—Fe_2O_3* Iron pyrites—FeS_2 Magnetite—Fe_3O_4*
Nickel	Millerite—NiS* Nickel glance—NiAsS*
Titanium	Ilmenite—FeO TiO_2* Rutile—TiO_2*

The minerals are invariably contaminated with rocky and earthy impurities termed *gangue*

13.2 METALLURGY

The process of obtaining or winning a metal in the free state from its ores is termed metallurgy of the metal concerned The various processes involved in metallurgy are :

(i) Benefication, concentration or dressing of the ore

(ii) Extracting the metal from the concentrated ore.

(iii) Refining of the metal so obtained

13 2-1 Methods Employed in the Concentration of Ores

(i) *Levigation* · Generally metal ores are heavier than the gangue associated with them. By flowing the powdered ore in a current of water the lighter rocky and earthy impurities can be washed away over much longer distances than the heavier ore particles The ore particles are left behind.

(ii) *Froth floatation method* This is one of the convenient methods used to concentrate sulphide ores In this method, the finely powdered ore is mixed with water. One or more frothing agents are added. Then air is blown through the mixture. A froth is formed. The ore particles rise to the surface, carried by the froth The earthy impurities are wetted by water and sink to the bottom. The froth is skimmed off Acid is added to break up the froth. The concentrated ore is filtered and dried.

(iii) *Liquation* This process is employed to concentrate ores having lower melting points than the impurities Thus the ore of antimony, stibnite, which has a low melting point, can be concentrated by heating the powdered ore on the sloping floor of a furnace. The temperature is adjusted to be just above the melting point of the ore. The ore melts and flows away Infusible impurities are left behind

(iv) *Leaching* In this method the powdered ore is treated with a suitable dissolving agent. It dissolves the ore but not the impurities. Thus bauxite, an ore of aluminium, besides Al_2O_3 contains impurities like $Fe_2O_3.SiO_2$. The powdered bauxite is leached with a strong solution of sodium hydroxide. Al_2O_3 dissolves forming sodium aluminate (Part I, Unit 13). The impurities remain undissolved. These are filtered off. From the sodium aluminate solution, $Al(OH)_3$ is precipitated. This is filtered, dried and ignited. Al_2O_3 is obtained in a pure form.

$Al_2O_3 + 6\ NaOH \longrightarrow 2\ Na_3AlO_3 + 3\ H_2O$
$Na_3AlO_3 + 3\ H_2O \longrightarrow 3\ NaOH + Al(OH)_3$
$2\ Al(OH)_3 \longrightarrow Al_2O_3 + 3H_2O$

Leaching is also employed to concentrate silver ores and to bring native gold into solution from rocks containing threads and particles of gold. In both cases, leaching is done using a dilute solution of sodium or potassium cyanide.

$Ag_2S + 4\ NaCN \longrightarrow 2Na[Ag(CN)_2] + Na_2S$
$4\ Au + 8\ KCN + 2H_2O + O_2 \longrightarrow 4K[Au\ (CN)_2] + 4\ KOH$

13.2-2 Extraction of Metals

A number of further steps are involved from the concentrated ore to the metal. These depend on the nature of impurities present and the metal compound in the ore. If the concentrated ore consists of a carbonate, a hydroxide, a hydrated oxide or a sulphide, it is first converted to an oxide form by either *calcination* or *roasting*.

Calcination is the process of heating an ore strongly so that volatile impurities are removed and the decomposable oxy-salts are converted to oxides Here presence of air is not essential nor it is necessary to exclude it. Some examples are :

$CaCO_3 \longrightarrow CaO + CO_2$
$Al_2O_3.2H_2O \longrightarrow Al_2O_3 + 2H_2O$
$2Al\ (OH)_3 \longrightarrow Al_2O_3 + 3H_2O$
$CuCO_3.\ Cu(OH)_2 \rightarrow 2CuO + H_2O + CO_2$
$CaCO_3.MgCO_3 \longrightarrow CaO + MgO + 2CO_2$

Roasting is the process of heating an ore in a controlled supply of air at a regulated temperature so that sulphur, arsenic and other elements present in a free or combined state are oxidized to volatile oxides and the metal oxide is left behind. Sometimes oxidation of sulphides is carried out only to the sulphate stage as in the case of lead. Some of the oxidation reactions of sulphide ores are given below.

$4FeS_2 + 11O_2 \longrightarrow 2Fe_2O_3 + 8SO_2$
$2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2$
$2PbS + 3O_2 \longrightarrow 2PbO + 2SO_2$
$PbS + 2O_2 \longrightarrow PbSO_4$
$2ZnS + 3O_2 \longrightarrow ZnO + 2\ SO_2$
$HgS + O_2 \longrightarrow Hg + SO_2$

From metal oxides metals are obtained by a process known as ***smelting***. This involves two main operations . ***reduction*** and removal of impurities as ***slag***. **Slag** is a *easily fusible material* formed by a combination of basic and acidic oxides. Reduction and slagging operation usually take place together. The substance added for formation of slag is called a ***flux***

Removal of impurities as slag

If the impurities are of acidic oxides, like SiO_2, P_2O_5, etc., lime is added as a basic flux to form fusible calcium silicate or phosphate

$$SiO_2 + CaO \longrightarrow CaSiO_3$$

$$P_2O_5 + 3CaO \longrightarrow Ca_3(PO_4)_2$$

For basic impurities, like MnO, silica acts as acidic flux.

$$MnO + SiO_2 \longrightarrow MnSiO_3$$

Reduction of oxides This is carried out in a number of ways

(i) ***Decomposition of oxide by heating*** : This is possible when the oxide is not thermally stable. Mercury is obtained from its sulphide ore, cinnabar (HgS), directly in the roasting step.

$$HgS + O_2 \longrightarrow Hg + SO_2$$

The recovery of metal is completed in a shaft furnance coupled with condensation chambers (Fig 13 1).

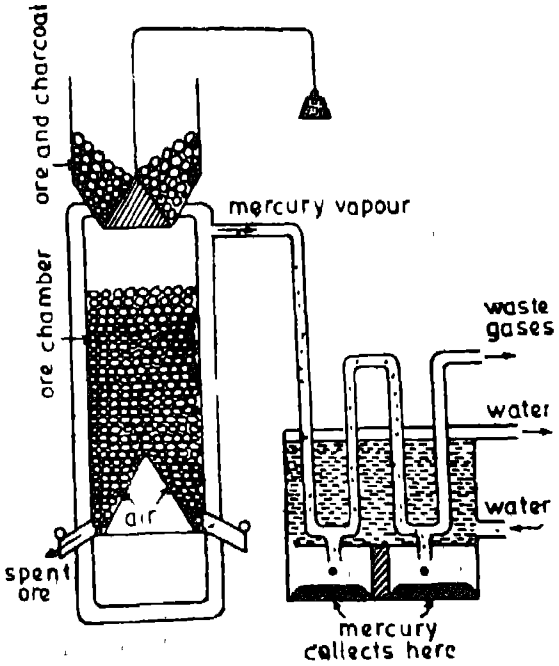

Fig 13.1 Extraction of mercury

(ii) ***Chemical reduction*** : A variety of reducing agents are used Carbon as charcoal, coal and coke, carbon monoxide, hydrogen, metals like sodium, aluminium, magnesium, etc., are some of the common reducing agents. In the case of certain sulphides the partly roasted ore is reduced to the metal by using the unchanged sulphide itself as the reducing agent. When carbon is used as the reducing agent, it is converted to carbon monoxide.

Examples of a few metals obtained by chemical reduction are given below

Tin is obtained from its oxide ore, *cassiterite* (SnO_2), by heating the concentrated ore with coke

$$SnO_2 + 2C \longrightarrow Sn + 2CO$$

Zinc is obtained from its sulphide ore, zinc blende (ZnS). The ore, concentrated by the froth floatation process, is roasted to the oxide and the oxide is reduced to the metal by heating with powdered coal in fire clay retorts (Fig. 13.2)

$$2ZnS + 3O_2 \longrightarrow 2ZnO + 2SO_2$$

$$ZnO + C \longrightarrow Zn + CO$$

$$2ZnS + 3O_2 \longrightarrow 2ZnO + 2SO_2$$

$$2ZnO + 2C \longrightarrow 2Zn + 2CO$$

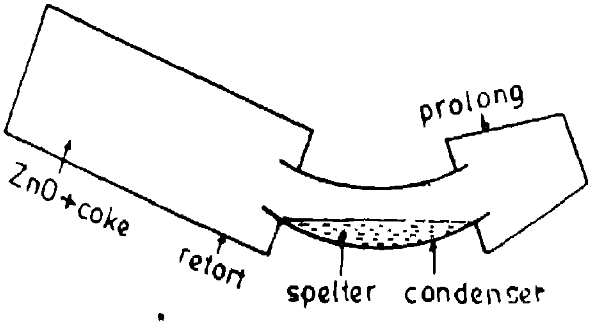

Fig 13.2 Extraction of zinc (ZnO is reduced to Zn metal when heated with coke in a fire clay retort The metal is obtained in the prolongs and earthenware condensers. Metal thus obtained is called spelter.)

Iron is obtained from its oxide ore, haematite. The powdered ore is sintered* to convert it into porous lumps It is then mixed with limestone pieces and coke pieces

The mixture is fed into a tall blast furnace (Fig. 13.3). Preheated air is used to obtain higher temperature by combustion of fuel in the bottom part of the furnace.

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* *Sintering* stands for melting of particles on the surface so that they hold together without loss in porosity. If the powder were used directly in the furnace, it will get close packed and gas passages will be blocked. The solid ore lumps are not used as such as they are too impervious for reducing agents to act on the inner parts of the ore.

This is required for melting the spongy iron formed in the upper parts of the furnace A series of reactions take place inside the furnace

$$CaCO_3 \longrightarrow CaO + CO_2$$

$$CO_2 + C \longrightarrow 2CO$$

$$2C + O_2 \longrightarrow 2CO$$

$$Fe_2O_3 + 3CO \longrightarrow 2Fe + 3CO_2$$

$$CaO + SiO_2 \longrightarrow CaSiO_3 \text{ (slag)}$$

Molten iron forms a layer below the slag layer of calcium silicate, During mel-

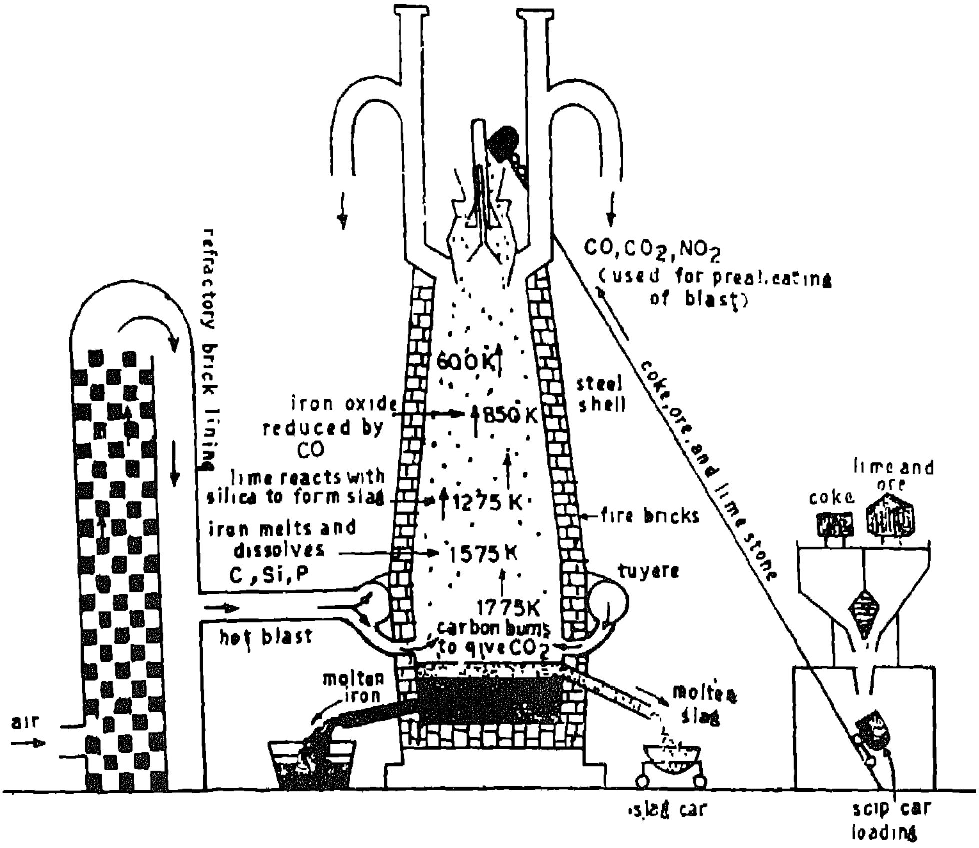


Fig. 13.3 (a) Schematic diagram of a blast furnace

ting, iron dissolves some corbon. The slag is removed from an upper hole on the side of the furnace and molten iron is run periodically out from a lower hole into sand moulds to give cast iron.

Fig. 13.3 (b) A photograph showing blast furnace of Bhilai steel plant (Courtesy : SAIL, Government of India enterprise)

The metals *manganese* and *chromium* are obtained from their oxides by reduction with aluminium powder. These oxides cannot be reduced by carbon or carbon monoxide. Since aluminium is more electropositive than manganese or chromium, it can reduce the oxides of these metals. The process is termed *aluminothermy*. The oxide formation in case of aluminothermy has the dual advantage of high temperatures and strong reducing action of aluminium.

$(\mathrm{MnO\ or\ Mn_3O_4}) + \mathrm{Al} \rightarrow \mathrm{Al_2O_3} + \mathrm{Mn}$

$\mathrm{Cr_2O_3} + 2\mathrm{Al} \rightarrow 2\mathrm{Cr} + \mathrm{Al_2O_3}$

The metals are obtained in molten state. Aluminothermy is used for in-place welding of large iron structures. A mixture of $\mathrm{Fe_2O_3}$ and Al-powder is taken in a crucible with a hole at the bottom. Magnesium ribbon imbedded in barium peroxide is used as igniter. The molten iron obtained is directly run into the crack (Fig 13.4).

$$\mathrm{Fe_2O_3} + 2\mathrm{Al} \longrightarrow 2\mathrm{Fe} + \mathrm{Al_2O_3}$$

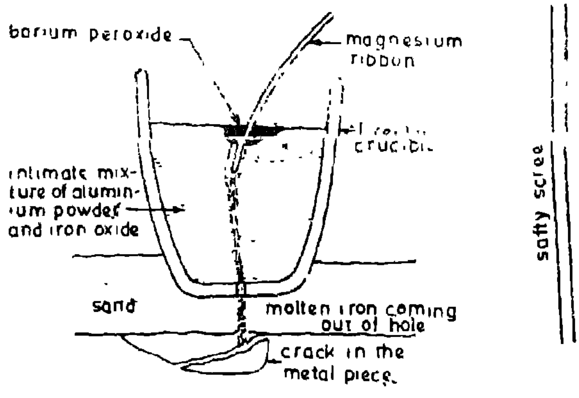

barium peroxide
magnesium ribbon
crucible
intimate mixture of aluminium powder and iron oxide
safty scree
sand
molten iron coming out of hole
crack in the metal piece

Fig. 13.4 Aluminothermy

Titanium is a metal specially important in space technology due to its lightness and high melting point.

The presence of even traces of oxygen could adversely affect the properties of titanium. So titanium is obtained by reducing pure $TiCl_4$ with magnesium.

$$TiCl_4 + 2\,Mg \longrightarrow Ti + 2MgCl_2$$

The metal copper is obtained from its sulphide ore, copper pyrites, $Cu_2S.Fe_2S_3$. The powdered ore is concentrated by the froth floatation process. During the roasting of the ore, iron sulphide is oxidized preferentially to FeO and is removed as $FeSiO_3$ (slag). Sand may be added to provide SiO_2. Molten sulphides form a separate layer. This mixture of sulphides rich in copper sulphide is called *matte*. Matte is heated in a low blast furnace to partially oxidize Cu_2S to Cu_2O. The air supply is now cut off and temperature of the furnace is raised. The unchanged Cu_2S reduces the Cu_2O formed to give impure copper. The chief reactions are given below ·

$$Cu_2S.Fe_2S_3 + 4O_2 \longrightarrow Cu_2S + 2FeO + 2SO_2$$

$$2FeO + 2SiO_2 \longrightarrow 2FeSiO_3$$

$$2Cu_2S + 3O_2 \longrightarrow 2\,Cu_2O + 2\,SO_2$$

$$2Cu_2O + Cu_2S \longrightarrow 6\,Cu + SO_2$$

(iii) *Electrolytic reduction* : Metals with high negative electrode potentials cannot be obtained by using chemical reduction methods. In such cases the reduction is carried out electrolytically The chief metals to be prepared by this method are the alkali and the alkaline earth metals. They are obtained by the electrolysis of their fused anhydrous halides. The preparation of sodium from sodium chloride can be represented as follows ·

$$2\,NaCl \xrightarrow{\text{fusion}} 2\,Na^+ + 2Cl^-$$

$$2\,Cl^- \longrightarrow Cl_2 + 2\,e^- \text{ (at the anode)}$$

$$2\,Na^+ + 2e^- \longrightarrow 2\,Na \qquad \text{(at the cathode)}$$

Extraction of sodium based on the above principles is utilized in an electrolytic cell shown in Fig. 11.1 of Part I of the textbook. Extraction of calcium and magnesium is shown in Fig. 13.5 and 13.6 respectively.

Pure alumina, Al_2O_3, obtained from bauxite ore is also reduced to the metal electrolytically. Al_2O_3, dissolved in molten cryolite ($3NaF.AlF_3$) in an iron box lined inside with electrically conducting carbon. This serves as the cathode. Carbon electrodes dipped into the electrolyte serve as anodes. The electrolyte has Na^+,

Al^{3+}, F^- and O^{2-} ions. On passing an electric current, Al^{3+} ions are discharged on the cathode and the O^{2-} ions at the anode. (Why are Na^+ and F^- ions not discharged ?) Molten aluminium sinks to the bottom of the box and is tapped out from there Some quantity of the oxygen formed escapes and some reacts with the anode to form CO_2. Hence the anodes have to be replaced from time to time. As aluminium and oxide ions decrease, the electrical conductance of the bath decreases. More alumina is periodically added. Thus electrolytic cell can operate for long times. Electrode reactions are :

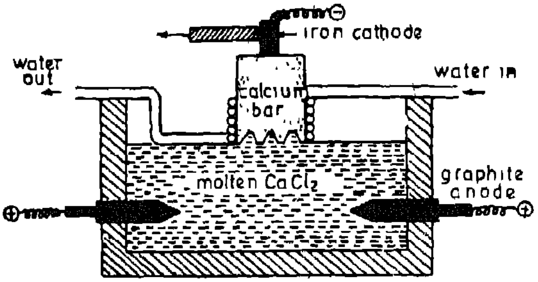


Fig. 13.5 : Extraction of Calcium

At the cathode $Al^{3+} + 3e^- \longrightarrow Al$

At the anode $2O^{2-} \longrightarrow O_2 + 4e^-$

$C + O_2 \longrightarrow CO_2$

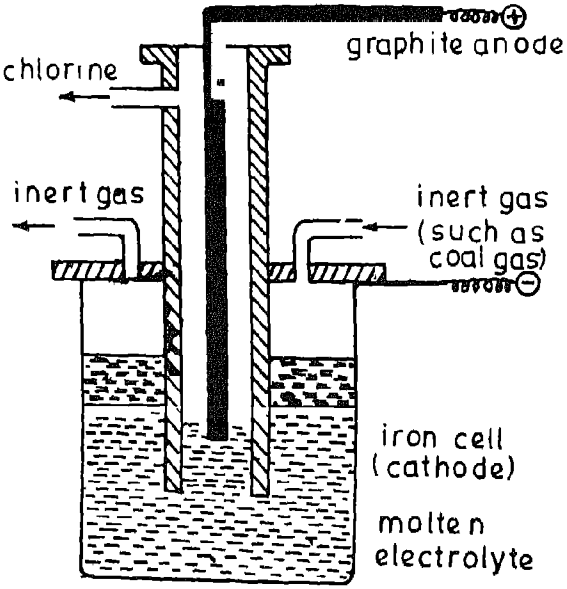


Fig 13.6 : Extraction of magnesium

The two reactions can be balanced for equalizing the numbers of electrons.

The cell used for production of aluminium, which is obtained as a result of electrolysis of alumina in molten cryolite is shown in Fig 13.1 in Part I of the textbook.

(v) *Some special techniques* · The metals silver and gold are obtained by the leaching-out process using a solution of potassium or sodium cyanide. From the argentocyanide or aurocyanide solutions, silver or gold may be precipitated by adding zinc dust A soluble cyanide complex of zinc is formed.

$$2Na[Ag(CN)_2] + Zn \longrightarrow Na_2[Zn(CN)_4] + 2Ag$$
$$2K[Au(CN)_2] + Zn \longrightarrow K_2[Zn(CN)_4] + 2Au$$

The choice of the metallurgical process for winning a metal from its ore depends on the nature of the ore, the availability and price of coal and electricity, the scale of operation and the value of the by-products obtained

The information about the extraction of some of the common metals is summarized in Table 13 2.

TABLE 13 2

Metal Extraction Techniques

Metal	*Reduction Electrode Potential (Volt)*	*Main Source*	*Main Method of Extraction*	*Equations*
Li	—3.04	Spodumene, $[LiAl(SiO_3)_2]$	Electrolysis of fused LiCl to which KCl is added	$Li^+ + e^- \longrightarrow Li$
K	—2.92	Carnallite, $KCl{\cdot}MgCl_2{\cdot}6H_2O$	Electrolysis of fused KCl to which $CaCl_2$ is added	$K^+ + e^- \longrightarrow K$
Ba	—2.90	Witherite ($BaCO_3$) Barytes ($BaSO_4$)	Electrolysis of fused $BaCl_2$	All preparations involve the reaction $M^{n+} + ne^- \longrightarrow M$
Ca	—2.87	Limestone ($CaCO_3$)	Electrolysis of fused mixture of $CaCl_2$ and CaF_2	
Na	—2 71	Rock salt (NaCl)	Electrolysis of fused mixture of NaCl and $CaCl_2$	
Mg	—2.37	Carnallite, Magnesite ($MgCO_3$)	Electrolysis of fused carnallite	
Al	—1.66	Bauxite ($Al_2O_3{\cdot}2H_2O$)	Electrolysis of Al_2O_3 dissolved in molten cryolite.	$Al^{3+} + 3e^- \longrightarrow Al$
Mn	—1.18	Pyrolusite (MnO_2)	Reduction of MnO_2 with aluminium powder	$4Al + 3MnO_2 \rightarrow 3Mn + 2Al_2O_3$
Ti	—0 95	Ilmenite ($FeO{\cdot}TiO_2$) Rutile (TiO_2)	Reduction of $TiCl_4$ with Na or Mg.	$TiCl_4 + 2Mg \rightarrow Ti + 2MgCl_2$
Zn	—0.76	Zinc blende (ZnS) Calamine ($ZnCO_3$) Zincite (ZnO)	Roasting ZnS to ZnO and reducing ZnO with carbon	$ZnO + C \rightarrow Zn + CO$

Metal	*Reduction Electrode Potential (Volts)*	*Main Source*	*Main Method of Extraction*	*Equations for Extraction*
Cr	−0.74	Chromite ($FeO.Cr_2O_3$)	Reduction of Cr_2O_3 with aluminium powder	$Cr_2O_3+2Al \rightarrow 2Cr+Al_2O_3$
Fe	−0.44	Haematite (Fe_2O_3)	Reduction of oxide with CO	$Fe_2O_3+3CO \rightarrow 2Fe+3CO_2$
Ni	−0.25	Millerite (NiS)	Reduction of NiO with CO	$NiO+CO \rightarrow Ni+CO_2$
Sn	−0.14	Tin stone or Cassiterite (SnO_2)	Reduction of SnO_2 with carbon	$SnO_2+2C \rightarrow Sn+2CO$
Pb	−0.13	Galena (PbS)	Reduction of PbO with C	$PbO+C \rightarrow Pb+CO$
Cu	+0.34	Copper pyrites ($Cu_2S\ Fe_2S_3$)	Partial oxidation of Cu_2S to Cu_2O	$2Cu_2S+3O_2 \rightarrow 2Cu_2O+2SO_2$
			Reduction of Cu_2O with unchanged Cu_2S	$2Cu_2O+Cu_2S \rightarrow 6\ Cu+SO$
Ag	+0.8	Free state, Argentite (Ag_2S)	Cyanide process	$Ag_2S+4NaCN \rightarrow 2Na[Ag(CN)_2]+Na_2S$ $2Na[Ag(CN)_2]+Zn \rightarrow Na_2[Zn(CN)_4]+2Ag$
Hg	+0.85	Cinnabar (HgS)	Partial thermal oxidation of HgS	$HgS+O_2 \rightarrow Hg+SO_2$
Pt	+1.2	Free state, Sperrylite ($PtAs_2$)	Thermal decomposition of $(NH_4)_2PtCl_6$	$(NH_4)_2PtCl_6 \rightarrow Pt+2NH_4Cl+3Cl_2$
Au	+1.5	Free state	Cyanide process	$4\ Au+8\ KCN+2H_2O+O_2 \rightarrow 4\ K[Au(CN)_2]+4\ KOH$ $2K[Au(CN)_2]+Zn \rightarrow K_2[Zn(CN)_4]+2Au$

13.3 REFINING OF METALS

The metals obtained from the ores are often associated with various impurities. The presence of impurities changes the physically useful properties of the metals. The process of purifying a metal is termed *refining*. Some of the methods used in the refining of metals are discussed here.

(i) ***Liquation*** : The method already described under methods for the concentration of ores (Sec. 13.2) can also be used as a method for refining metals of low melting points. Crude tin obtained from reduction of tinstone may contain some insoluble and non-metallic impurities. By heating such tin (m.p.=505K) on the sloping floor of a furnance purer molten tin flows down, leaving the impurities behind.

(ii) ***Cupellation*** : This is a method employed to purify silver containing lead as an impurity. The impure silver is heated in a shallow vessel made of bone-ash under a blast of air. The lead is easily oxidized to powdery lead monoxide Most of it is carried away by the blast of air The rest melts and is absorbed by the bone ash cupel. Pure silver is left behind. Silver itself is not oxidized under these conditions

Poling · This is a method for removing impurities of reducible oxides from the respective metals. Blister copper contains a little cuprous oxide This is removed by stirring the molten blister copper with green poles of wood. The gases escaping from wood act as reducing agents They reduce the oxide to the metal. To prevent re-oxidation by air, the surface of the molten copper is covered with a layer of powdered charcoal.

(iv) *Electrolytic refining* : This is a very convenient method for refining many impure metals. Blocks of impure metal form the anode and thin sheets or wires of the pure metal form the cathode A solution of a salt of the metal serves as the electrolyte. On passing an electric current through the electrolyte, the pure metal is deposited on the cathode from the electrolyte. At the same time more ions of the metal enter the electrolyte by oxidation of the anode. The impurities present in the anode either dissolve in the electrolyte or collect as a muddy deposit (anode mud) below the anode. Thus in the electrolytic refining of copper, impurities of iron and zinc are dissolved in the electrolyte (Why are they not deposited on the cathode along with copper ?) and while gold, platinum and silver are left behind as anode mud (Fig. 13 7)

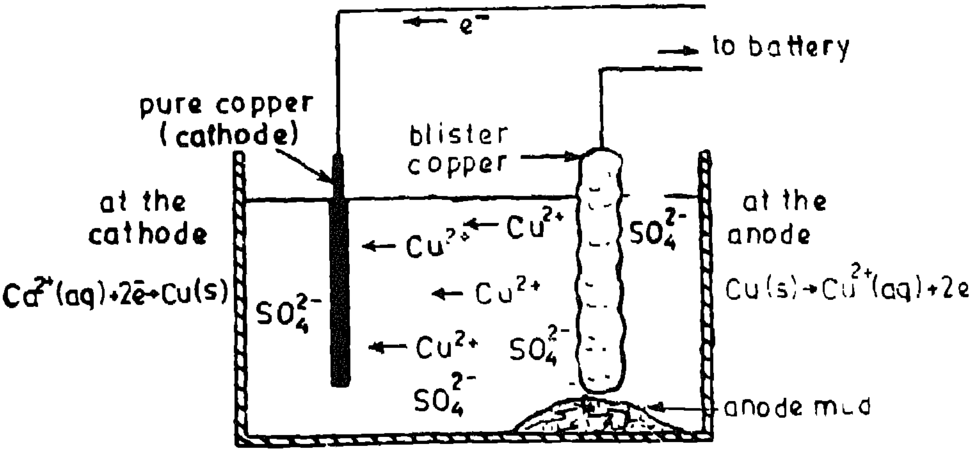


Fig 13.7 Electrolytic refining of copper

(v) *Zone refining* . This is a method developed for preparing highly pure metals It is based on the principle that an impure molten metal on solidification will deposit crystals of the pure metal and the impurities will stay behind in the molten part of the metal The impure metal is taken in the form of a rod. A narrow region is melted at one end The molten region is progressively transferred from one end of the rod to the other by slowly moving the source of heat. Impurities collect in the molten part and are progressively swept to one end of the metal. The process can be repeated Pure germanium is obtained by this method (When will this method fail ?).

(vi) *Van Arkel method* This is also a method for getting ***ultra-pure* metals.** The principle involved is to convert the metal to a volatile unstable compound and to subsequently decompose it to give the pure metal. The impurities present should be such as not to be affected. Metals like titanium, zirconium, etc. are purified by using this method.

13.4 ROCKS AND MINERALS

The individual portions of the earth's crust are made up of mixtures of minerals. These portions are referred to as *rocks*.

Rocks are generally classified into three types.

(i) *Igneous rocks* · Well within the earth, there would be molten material called *magma* By pressure changes, liquid magma is forced higher up into the crust regions. It may cool and solidify before reaching the surface of the earth. The rocks thus formed directly from the molten magma are termed *Igneous* rocks. Quartz, felspar, mica and magnetite are some of the minerals associated with igneous rocks

(ii) *Sedimentary or secondary rocks* : These rocks are derived from pre-existing rocks The earlier rocks are broken down by frost, rain, wind, rivers or by sea action. The materials thus formed are moved from their places of origin and deposited elsewhere as sediments. These become firm with lapse of time and form sedimentary rocks. Sedimentary rocks are also produced by accumulation of organic materials and the drying up of waters of seas. Dolomite, salt deposits, limestone, siliceous deposits, coal, etc. constitute sedimentary rocks.

(iii) *Metamorphic rocks* . Such rocks result from changes in pre-existent rocks brought about by changes of pressure and temperature. Under the new pressures and temperatures the original materials are not stable. So they change into modified minerals stable under the new conditions. Garnet, kyanite, sillimanite, etc. are examples of metamorphic minerals.

13.5 MINERAL WEALTH OF INDIA

All minerals and mineral products are derived from rocks. Minerals are indispensable in the life of man. The mineral wealth of a country is a measure of its prosperity. Fortunately, our country is quite rich in a variety of minerals.

There is an uneven territorial distribution of the mineral wealth in India. The alluvial plain of Northern India are practically devoid of economically useful minerals. Bihar and Orrissa have large deposits of ores of iron, manganese, copper, thorium, uranium, aluminium, chromium, besides deposits of coal, mica, sillimanite and phosphates. Next to Bihar and Orissa comes Madhya Pradesh with good reserves of iron and manganese ores, limestone, bauxite and coal. Tamil Nadu had sizable deposits of iron and manganese ores, magnesite, mica, limestone and lignite. Karnataka besides having a monopoly of supplying gold, has iron and chrome ores. Andhra Pradesh has good reserves of second quality coal. Kerala leads in the matter of mineral sands of strategic importance like the monazite and the ilmenite besides rutile and garnet. Rajasthan is rich in non-ferrous metals like copper, lead and zinc besides uranium, mica, beryllium. Precious stones like aquamarine and emerald are also mined in Rajasthan. Gujarat, Assam, and Maharashtra are rich in petroleum. Coal is the main mineral from West Bengal Kashmir has deposits of coal and aluminium ore. Sikkim has magnesite deposits and also copper and iron ores.

EXERCISES

13.1 Define the following terms :

(a) Mineral
(b) Ore
(c) Gangue
(d) Flux
(e) Slag
(f) Calcination
(g) Roasting
(h) Smelting

13.2 What is ore dressing ? What are the methods employed in ore dressing ?

13.3 ZnO can be reduced to the metal by heating with carbon but not Cr_2O_3. Why is it so ?

13.4 What is electrolytic refining ?

13.5 Explain the principles involved in obtaining (i) aluminium from bauxite, and (ii) coppe
from copper pyrites.

13.6 **What is cupellation ?**

13.7 **What is Van-Arkel method ?**

13.8 **How are rocks classified ? Give examples**

13.9 **What is zone refining ?**

13.10 **Explain :**

(i) Forth floatation, and

(ii) Cyanide process

13.11 **How may impurities be removed in the following cases .**

(i) An impurity of Cu_2O in copper metal,

(ii) An impurity of carbon in iron,

(iii) An impurity of copper in silver,

(iv) An impurity of platinum in copper, and

(v) An impurity of insoluble sand and other particles in liquid mercury

UNIT 14

Transition or *d*-Block Elements

The element like hydrogen, the alkali and alkaline earth metals, and the elements of boron, carbon, nitrogen, oxygen and fluorine families and the rare or noble gases of zero group elements are together known as the *Major* or *Representative elements* of the Periodic Table Some of them belong to the *s*-block and the others to the *p*-block of elements This grouping follows from the last or characterizing electron of the element entering an *s* or a *p*-orbital of outer most energy shell The elements to be discussed in the present Unit will be those in which the characterizing or distinguishing electron of the elements will be filling up a *d*-orbital with principal quantum number one less than the *s*-orbital already filled. Table 14,1 shows the three complete series of *d*-block elements and actinium which is at the beginning of the fourth series.. A few of the elements in this series have been made in the laboratory but they have not been fully characterized and hence are not shown here

All elements of *d*-block are metals. They include the most coveted metals, the gold and the other precious metals, like silver and platinum Copper is industrially important and iron is extremely important for the structural strength and found in abundance. The wonder metal of our times. titanium, is also here.

A look at Table 14.1 shows that a number of elements have anomalous electronic configurations They belie the simple electron filling rules. This is so because in these elements with larger atomic energy shells the orbital energies of the *ns* and (n-1) *d* orbitals become too close together to be governed by the simple generalizations alone

14.1 DEFINITION AND ELECTRONIC CONFIGURATIONS

The transition in properties and from basic to acidic behaviour of oxides in a period, is well marked in case of *s* and *p*-elements of the period as is observed for

TABLE 14.1

d-Block Elements

21 Sc [Ar] $4s^2 3d^1$	22 Ti $4s^2 3d^2$	23 V $4s^2 3d^3$	24 Cr* $4s^1 3d^5$	25 Mn $4s^2 3d^5$	26 Fe $4s^2 3d^6$	27 Co $4s^2 3d^7$	28 Ni $4s^2 3d^8$	29 Cu* $4s^1 3d^{10}$	30 Zn $4s^2 3d^{20}$
39 Y [Kr] $5s^2 4d^1$	40 Zr $5s^2 4d^2$	41 Nb* $5s^1 4d^4$	42 Mo* $5s^1 4d^5$	43 Tc* $5s^1 4d^6$	44 Ru* $5s^1 4d^7$	45 Rh* $5s^1 4d^8$	46 Pd* $5s^0 4d^{10}$	47 Ag* $5s^1 4d^{10}$	48 Cd $5s^2 4d^{10}$
57 La [Xe] $6s^2 5d^1$	72 Hf $6s^2 5d^2$	73 Ta $6s^2 5d^3$	74 W $6s^2 5d^4$	75 Re $6s^2 5d^5$	76 Os $6s^2 5d^6$	77 Ir $6s^2 5d^7$	78 Pt* $6s^1 5d^9$	79 Au* $6s^1 5d^{10}$	80 Hg $6s^2 5d^{10}$
89 Ac [Rn] $7s^2 6d^1$	104	105	106	107	108	109	110	111	112

*Anomalous configurations.

All elements in a row have a core electronic configurations of the noble gas shown for the first element in the row

the Li and Na periods It is because the energies of the *s*- and *p*-orbitals are markedly different. In the case of *d*-orbitals not only are the energies very closely similar for the *d*-orbitals of the same shell but also they are similar to the energies of the *s*-and *p*-orbitals of the next higher principal quantum number. The *d*-orbitals easily hybridize with the *s*-and *p*-orbitals of the next higher principal quantum numbers. The transition in properties as the *d*-orbitals of a shell are filling up is very gradual. This gradation is observed in case of the first series of *d*-block elements beginning with scandium but becomes less marked for the other two series. Various attempts to find a common feature of those elements to be used as a definition for the transition elements have not been quite successful. Following definition may however be considered as one of the possibles

Transition metals are those elements, at least one of whose simple ions has an incomplete outer shell of d-electrons containing between 1 and 9 electrons.

This definition is also not without exceptions.

That some of the electronic configurations shown in Table 14.1 are anomalous is due to simple rules for electron filling being not quite enough. These configurations are based on experimental evidence of atoms and can change during formation of ions and molecules. The 10 columns or groups amongst the *d*-block elements are due to there being five *d*-orbitals in energy shells and each of these orbitals can accomodate two electrons.

14 2 GENERAL CHARACTERISTIC PROPERTIES

(i) *Similarities in properties* : The *d*-block elements show some horizontal similarity in properties in contrast to the elements of *s*-and *p*-blocks. They show vertical group similarities like the other elements.

(ii) *Metallic character* : They are all metals. They show a gradual decrease in electropositive character upto the elements in the copper group. Zinc group elements are distinctly more reactive. In general these metals exhibit even less reactivity than they are expected to According to their electrode potentials they should displace hydrogen from acids but they do not do so. It is because of their surfaces being covered with insoluble, relatively inert and sticking oxides. Chromium is a very important corrosion resisting metal.

(iii) *Variable valency* : They show in general variable oxidation states These multiple oxidation states of an element differ by units of one (Table 14.2). Some *p*-block elements also show multiple oxidation states but they differ usually by units of two. Zero and negative oxidation states are possible only in complexes.

TABLE 14.2

Some Properties of First Row *d*-block Elements

Element	*Electronic configurations ($Ar3d^x$-$4s^y$)*	*Number of unpaired d-electrons+total s-electrons*	*Density (g/cm^3)*	*Atomic radius (Å)*	*Melting point (K)*	*Boiling point (K)*	*First ionization energies kJ mol^{-1}*	*Electronegativities (Pauling's)*	*Stable oxidation states*
Sc	d^1s^2	3	3.01	1.64	1812	3003	633	1.30	3
Ti	d^2s^2	4	4.51	1.47	1941	3533	659	1.40	4,3
V	d^3s^2	5	6.10	1.35	2173	3723	650	1 60	5,4,3
Cr	d^5s^1	6	7.19	1.30	2148	2753	653	1.88	6,3,2,
Mn	d^5s^2	7	7.43	1.35	1518	2370	713	2.07	7,4,2
Fe	d^6s^2	6	7.86	1.26	1809	3273	762	2.10	3,2,0
Co	d^7s^2	5	8.90	1.25	1768	3173	759	2.10	3,2,0
Ni	d^8s^2	4	8.90	1.25	1726	3303	736	2.10	2,0
Cu	$d^{10}s^1$	3	8.92	1.28	1356	2868	745	2 60	2,1
Zn	$d^{10}s^2$	2	7.14	1.37	692	1180	906	2 84	2

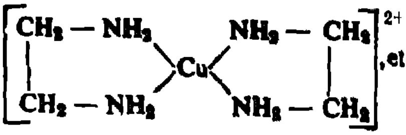
(iv) *Gradation in properties* : The effect of adding an electron to an inner shell orbital is not so well marked as for such addition to an outer *s*-or *p*-orbital. This is shown by a rather gradual decrease in atomic radii and a slow increase in first ionization energies and electronegativities. The melting and boiling points also change but not so regularly (Table 14.2).

(v) *Catalytic activity* : These elements and some of their compounds show catalytic activity. It is mostly attributed to the elements easily passing from one valence state to another. Iron, nickel and platinum are important metallic catalysts. Vanadium pentoxide is used in the contact process for making sulphuric acid.

Decomposition of bleaching powder is catalyzed by cobalt salts in aqueous solutions.

$$Co^{2+} + OCl^- + H_2O \longrightarrow Co^{3+} + Cl + 2OH^-$$

$$2Co^{3+} + 2OH^- \longrightarrow 2Co^{2+} + \tfrac{1}{2} O_2 + H_2O$$

(vi) *Complex ion formation* : *d*-block elements easily form complex ions and molecules due to the presence of empty and partially filled orbitals. The empty *d*-orbitals can hybridise with *s* and *p* orbitals of next higher shell and in turn result into complex formation. Coordination complexes with structures like $[Fe(CN)_6]^{4-}$, $[Fe(CN)_6]^{3-}$, $[Cu(NH_3)_4]^{2+}$; $[Ag(NH_3)_2]^+$, $Ni(CO)_4$,  ,etc. are quite common. Complexes are chemical combinations in which a *central* atom (usually a metal) or ion is surrounded by a number of other molecules or ions which are already formed in a normal way. The surrounding ions or molecules are called *ligands*. The attachment of ligands to the central atom is by co-ordinate bonds. The number of attached ligands is called the *coordination number* (abbreviated to C.N.) of the central ion in a particular combination. The complex ions dissociate to a lesser or greater extent into the component units. If a central atom is attached to a ligand at only one point, such ligand is called monodentate. Thus CN^-, NH_3, CO, H_2O, are some of the examples of monodentate ligands. Ethylene diamine (NH_2-CH_2-CH_2-NH_2) can attach on both amino groups to a single Cu^{2+} ion. This is a bidentate ligand. Ter-, quadri-and some higher order ligands are also known. The capacity of a multidentate ligand to surround a central ion by catching it at more than one points is called *chelation* and the complexes so formed are called *chelates*. Ethylene diamine forms chelate complexes.

(vii) *Interstitial compounds* : The *d*-block elements may not only take up atoms of small size in the vacant spaces in their lattices but even bond with them to form hard and rigid structures. Thus steel and cast iron are hard because of interstitial compound formation with carbon. Interstitial presence of other atoms in a metal obstructs the sliding of atoms in the metal and the properties of malleability and ductibility are lost to a lesser or greater extent. At the same time tenacity of the metal increases.

(viii) *Alloy formations* . Since *d*-block elements are quite similar in atomic sizes, they can mutually substitute one another in crystal lattices This gives solid solutions and smooth alloys. Such alloys are hard and yet workable and have often higher melting points. Chromium, vanadium, molybdenum, tungsten and manganese steels and the stainless steel belong to this group of alloys.

(ix) *Formation of coloured ions* : Compounds containing unpaired electrons usually absorb light in the visible range and are thus coloured. Table 14.3 gives relationships between absorbed and emitted (observed) colours. These are pairs of complimentary colours*. Colours of some normal complexes are given in Table 14.4.

TABLE 14.3

Observed and Absorbed Colours of Substances

Absorbed Colour	*Observed Colour*
Infrared	White
Red	Blue-green
Orange	Blue
Yellow	Indigo
Yellow-green	Violet
Green	Purple
Blue-green	Red
Blue	Orange
Indigo	Yellow
Violet	Yellow-green
Ultraviolet	white

TABLE 14.4

Colours of Some Complexes

$[Co(H_2O)_6]^{2+}$	Pink
$[Cr(H_2O)_6]^{3+}$	Violet
$[Cu(H_2O)_4]^{2+}$	Light blue
$[Cu(H_2O)_2(NH_3)_4]^{2+}$	Dark blue
$[Fe(CN)_6]^{4-}$	Yellow
$[Fe(CN)_6]^{3-}$	Orange-red
$[Ni(H_2O)_6]^{2+}$	Green
$[Ni(NH_3)_6]^{2+}$	Blue

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* Two colours are said to be complimentary if lights of these colours mix together to give white light.

(x) *Paramagnetism in d-block elements* : Ions, atoms and molecules which have unpaired electrons in their orbitals make the concerned substances paramagnetic. Such substances weigh more when a magnetic field is applied to them. Paramagnetism is quite common in elements and compounds of *d*-block elements. Paramagnetism increases as the number of unpaired electrons increases in the constituent particles of a substance. Table 14.5 gives the magnetic moments of some of the ionic species

TABLE 14.5

Magnetic Moments of Some Ionic Species

Ion	*Electronic configuration*	*Number of unpaired electrons*	*Magnetic moment*, μ (*Bohr Magneton*)
Ti^{3+}	d^1s^0	1	
V^{3+}	d^2s^0	2	2.75
Cr^{3+}	d^3s^0	3	3.80
Mn^{2+}	d^5s^0	5	5.85
Fe^{2+}	d^6s^0	4	5·10
Fe^{3+}	d^5s^0	5	5.85
Cu^{+}	$d^{10}s^0$	0	0·0
Cu^{2+}	d^9s^0	1	1.95
Zn^{2+}	$d^{10}s^0$	0	0.0

(xi) *Isomerism* : Some of the compounds of *d*-block elements show geometrical and optical isomerism. We will learn about these isomerisms in Unit 16 of organic portion. However, it is not possible to say more about isomerism in inorganic compounds in the present course.

14.3 RULES FOR NOMENCLATURE OF COMPLEXES

(1) Non-ionic complexes are given a one word name. In ionic complexes, cations and the anions are named separately, the cation first and then the anion.

(2) Neutral ligands are named as the molecules. Negative ionic ligands having *e* at the end of their names are changed to *o*. Names of positive ionic ligands end in -*ium*. However, some ligands keep their conventional names, even though violating the rule. Examples of ligand names are :

H_2O, aquo; NH_3, ammine; CO, carbonyl;
NO, nitrosyl;
$NH_2 - CH_2 - CH_2 - NH_2$, ethylene diamine.
F^-, fluoro;

Cl^-, chlor*o*—;
Br^-, bromo—;
OH^-, hydrox*o*,
CN^-, cyan*o*;
$C_2O_4^{2-}$, oxalat*o*;
NCS^-, thiocyanat*o*
$[NH_2-NH_3]^+$, hydraz*inium*

(3) The ligands in a complex are named first and in the order, anionic ligands, neutral ligands and cationic ligands. The names run together as one word. Within each group of ligands, they are written in an order of increasing complexity. The number of identical ligands is shown by prefixes di-, tri-, tetra-, etc., for simple insubstituted ligands and by bis-, tris, tetrakis, etc, for substituted complex ligands. The name of the central atom in a complex is given after and in continuation with the names of ligands and its oxidation state, if any, is indicated immediately after in brackets by a Roman numeral. The name of the central atom is kept unchanged if the complex is a cation or a neutral molecule. If the complex is an anion, the name of the central atom is followed by the suffix, -*ate*.

EXAMPLES

$K_3[Fe(CN)_6]$	Potassium *hexa*cyan*o*ferr*ate* (III) cation anion
$K_4[Cu(CN)_6]$	Potassium *hexa*cyan*o*cupr*ate* (II)
$K[Ag(CN)_2]$	Potassium *di*cyan*o*argent*ate* (I)
$K_2[HgCl_4]$	Patassium *tetra*chlor*o*mercur*ate* (II)
$[Pt(NH_3)_3(NO_2)Cl_2]Br$	*Di*chloronitro*tri*ammineplatinum (IV) bromide cation anion
$[\{(C_6H_5)_3P\}_3Rh]Cl$	*Tris* (*tri*phenyl phosphine) rhodium (I) chloride cation anion
$[Cu(H_2O)_2(NH_3)_4]SO_4$	*Di*aquotetraammine copper (II) sulphate

14.4 APPLICATION OF COMPLEX FORMATION

Complexes and complex formation methods have been found useful in a number of ways. Some of these are briefly described here

(i) *Dyeing* : Mordants are insoluble substances which are uniformly deposited in the fibres to be dyed. These can then attach to the molecules of dyes by complex formation and help in fixing the dye to the fibres in a stable form. Notable mordants are $Fe(OH)_3$ and $Al(OH)_3$.

(ii) *Control of ion concentration* Availability of a dissolved electrolyte in a non-ionic state can be conveniently arranged through complex formation. Thus in the electroplating baths large amount of silver is held as $K[Ag(CN)_2]$ which provides very little Ag^+ ions as such but can provide all the silver for electroplating. The ionization of $[Ag(CN)_2]^-$ to give Ag^+ and CN^- ions is very low.

During qualitative and quantitative analysis, concentrations of certain ions can be so reduced as not to respond to addition of a reagent. The non-complexing ions or less complexing ions can then be detected and estimated. This application is called the *masking* of ions.

KCN is used as a masking agent for Cu^{2+} ions when testing for Cd^{2+} ions. Cu^{2+} ions form tricyanocuprate (I) ions, $[Cu(CN)_3]^{2-}$, which ionize less than the tetracyano cadmiate (II), $[Cd(CN)_4]^{2-}$ ions.

Polyphosphates can keep Ca^{2+} ions of hard water in dissolved state and prevent scale formation in boilers. EDTA salt (sodium ethylene*d*iamine*t*etra*a*cetate) is used in complexometric titrations. Dimethyl glyoxime is used for estimating nickel as an insoluble complex.

14.5 METALS OF SCANDIUM, TITANIUM AND VANADIUM GROUPS

Titanium (Ti) and zirconium (Zr) are the most abundant metals of this group Titanium is important for making light weight stable alloys. They have high tensile strengths TiO_2 and ZrO_2 are used as extra white hard paint pigments. $TiCl_4$ is a liquid boiling around 409K. Its vapour reacts with moisture to form TiO_2 and HCl This titanium tetrachloride is used for producing dense white smoke screens and for making writings in the sky

14 6 METALS OF CHROMIUM AND MANGANESE GROUPS

Chromium (Cr) and manganese (Mn) are the most important metals of their respective groups. Molybdenum (Mo) and tungston (W) are other useful metals of chromium group. Tungsten is used for making filaments of electric bulbs as it can be heated to white heat without evaporation or losing shape. Molybdenum is used as a catalyst in the Haber's process for manufacturing ammonia. Technetium (Tc) does not occur in nature Chromium is avilable in enough quantities for large scale electroplating or chrome plating of other metals. It provides a scratch resisting, non-rusting highly shining protective coating. Chromium and manganese are useful in making useful alloy steels Either or both of them may be used for making stainless steel

Chromium and manganese compounds are important in several oxidation-reduction systems.

14.6.1 CHROMIUM COMPOUNDS

Most of these compounds are coloured. The element gets its name on this account (Greek *chroma* means colour). Most important chromium compound is *potassium dichromate*, $K_2Cr_2O_7$. It has orange-red crystals. It is made by mixing hot saturated solutions of sodium dichromate and potassium chloride in equimolecular proportions.

$$Na_2Cr_2O_7 + 2KCl \longrightarrow K_2Cr_2O_7 + 2NaCl$$

Sodium chloride being the least soluble of these substances separates and is filtered off On cooling, crystals of $K_2Cr_2O_7$ are formed. Some of its important reactions are :

$$K_2Cr_2O_7 + 4NaCl + 6H_2SO_4 \xrightarrow{\text{heat}} 2KHSO_4 + 4NaHSO_4 + 3H_2O + 2CrO_2Cl_2$$

This reaction is used as a test for chlorides due to easily recognised red vapour of *chromyl chloride*, CrO_2Cl_2

$$K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3[O]$$

The oxygen available in acidified solutions can be used for various oxidation reactions. A few examples are cited below.

With Iodides

$$2HI + [O] \longrightarrow H_2O + I_2$$

With ferrous salts

$$2FeSO_4 + H_2SO_4 + [O] \longrightarrow Fe_2(SO_4)_3 + H_2O$$

$$\text{or } 2Fe^{2+} + [O] + 2H^+ \longrightarrow 2Fe^{3+} + H_2O$$

With sulphites : $SO_3^{2-} + [O] \longrightarrow SO_4^{2-}$

With sulphides : $S^{2-} + [O] + 2H^+ \longrightarrow H_2O + S$

In alkaline solutions dichromate ions are converted to chromate ions

$$Cr_2O_7^{2-} + 2OH^- \longrightarrow 2CrO_4^{2-} + H_2O$$

Acidification reverses this reaction.

$$2CrO_4^{2-} + 2H^+ \longrightarrow Cr_2O_7^{2-} + H_2O$$

In solution, dichromate ions react with water to give a small concentration of chromate ions :

$$Cr_2O_7^{2-} + H_2O \longrightarrow 2CrO_4^{2-} + 2H^+$$

Ammonium dichromate when initially heated undergoes **an exothermic decomposition** with sparks (Fig. 14 1). This reaction is known as ***chemical valcano.***

$$(NH_4)_2Cr_2O_7 \longrightarrow \underset{\text{green light powder}}{Cr_2O_3} + 4H_2O + N_2 + \text{heat}$$

Formation of nitrogen provides the eruption effect

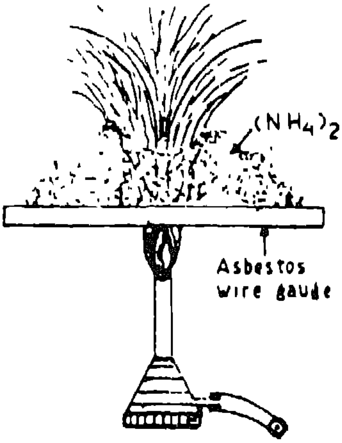

Fig. 14 1 Chemical valcano

Uses

Potassium dichromate is, a very useful titrant for estimating ferrous compounds, iodides and sulphites. It is the starting material for making other chromium compounds like chrome alum, $K_2SO_4.Cr_2(SO_4)_3.24\,H_2O$. It is used in photography for hardening gelatine film and in dyeing for providing $Cr(OH)_3$ as mordant.

The cleansing mixture used in laboratories for cleaning glassware consists of concentrated sulphuric acid and some crystals of $K_2Cr_2O_7$. It acts slowly and oxidizes greasy substances. *It loses its effectiveness when the acid gets diluted.*

14.6·2 MANGANESE COMPOUNDS

The most stable valence state of manganese is +2 Hydrated Mn^{2+} ions impart a light pink colour to the salts. From point of view of usefulness and commercial value, the most important manganese compound is *potassium permanganate*. Pyrolusite is the mineral form of MnO_2 It is fused with KOH in air to form green potassium manganate, K_2MnO_4

$$2MnO_2 + 4KOH + O_2 \xrightarrow{\text{heat}} 2K_2MnO_4 + 2H_2O$$

Potassium manganate is oxidized electrolytically or by passing ozone into solution.

$$\underset{\text{green}}{MnO_4^{2-}} \longrightarrow \underset{\text{purple}}{MnO_4^-} + e^- \qquad \text{(anode reaction)}$$

$$2MnO_4^{2-} + O_3 + H_2O \longrightarrow 2MnO_4^- + 2OH^- + O_2$$

When the solution is concentrated by evaporation, $KMnO_4$ crystallizes.

Oxidation of Mn^{2+} ions is carried out quickly and quantitatively to MnO_4^- by warming with sodium bismuthate in excess of nitric acid :

$$2Mn^{2+} + 5NaBiO_3 + 14H^+ \longrightarrow 2MnO_4^- + 5Na + 5Bi^{3+} + 7H_2O$$

Permanganate ion is almost the best oxidizing agent. It oxidizes H_2S, SO_2, sulphites, thiosulphates, nitrites, iodides, bromides, chlorides and ferrous salts

In acid media the reaction on adding a reducing agent is :

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$$

or $$2KMnO_4 \equiv K_2O + 2MnO + 5\,[O]$$

In alkaline media, MnO_2 is formed from $KMnO_4$ when a reducing agent is added

$$2KMnO_4 \equiv K_2O + 2MnO_2 + 3[O]$$

or $$MnO_4^- + 4H^+ + 3e^- \longrightarrow MnO_2 + 2H_2O$$

In neutral aqueous solutions also a similar change takes place when a reducing agent is added. Its action on oxalic acid or oxalate solutions acidified with dilute H_2SO_4 is autocatalyzed by Mn^{2+} ions .

$$H_2C_2O_4 + [O] \longrightarrow H_2O + 2CO_2$$

Permanganate solution in water decomposes slowly on exposure to light depositing brown MnO_2.

$$4MnO_4^- + \underset{\text{(from water)}}{4H^+} \xrightarrow{\text{light}} 4MnO_2 + 3O_2 + 2H_2O$$

In concentrated alkalies permanganate gives manganate, MnO_2 and oxygen.

$$2KMnO_4 \longrightarrow K_2MnO_4 + MnO_2 + O_2$$

With concentrated sulphuric acid, it gives covalent, highly explosive green oily Mn_2O_7. (This reaction is extremely dangerous and should not be attempted) On heating to 523K potassium permangnate decomposes to potassium manganate, MnO_2 and O_2.

Uses

It is used as an oxidizing agent in the laboratory and in the industry It is a convenient volumetric oxidant for estimating ferrous salts, oxalates and other reducing agents It is used for disinfecting well water.

14 7 METALS OF GROUP VIII (IRON GROUP)

Metals of this group form three triads Several important metals belong to this group Some of these are iron (Fe), cobalt (Co), nickel (Ni) We also know of platinum (Pt) as a noble metal and as an important catalyst. Palladium is now becoming better known for white jewellery A thin plating of palladium on silver articles prevents the tarnishing of silver Palladium is not affected by atmospheric H_2S.

Like gold, platinum dissolves in aqua regia to form H_2PtCl_6 Without complex formation the metal may not be attacked by the oxyacids.

Here we shall restrict ourselves to the study of some of the important facts about iron Chemical changes occurring in the extraction of iron metal from oxide ore has been described in Unit 13

14.7-1 IRON AND STEEL

Iron obtained from the blast furnace contains about 5 per cent carbon. It is called *pig iron* It is also called *cast iron* as it gives good castings. Cast iron expands slightly on cooling Cast iron is resistant to corrosion and is used for sewage pipes However, it is quite brittle and very weak for structural uses. A more useful form of iron is *steel*. It is an alloy of iron and carbon in which the proportion of carbon may vary from about 0 2 to 2.0 per cent. When the carbon content of iron falls below 0.2 per cent, iron is regarded as almost pure It is easiest to work with this form of iron It is soft, malleable, easy to weld but is structurally weak and cannot be magnetised permanently. This pure form of iron is called *wrought iron*. It is used for making chains, wires and electromagnets. These magnets lose magnetism as soon as the electric field is withdrawn

For making steel from cast iron, the carbon content has to be brought down from about 5 per cent to between 0 2 to 2 per cent according to the quality of steel to be made. The melting points of iron rises as its carbon content is lowered The carbon content can be decreased by burning away the carbon The furnance used for this purpose is called a convertor (Fig 14 2) The oxygen blown process is the one more in use now. This goes by the name of L. D. process or Linz—Donawitz* process In this method a very fast jet of oxygen is blown on the surface of molten cast iron. Due to oxidation of impurities, the temperature rises to 2300 to 2800 K. Impurities of carbon, silicon and manganese are oxidized to their respective oxides SiO_2 is slagged

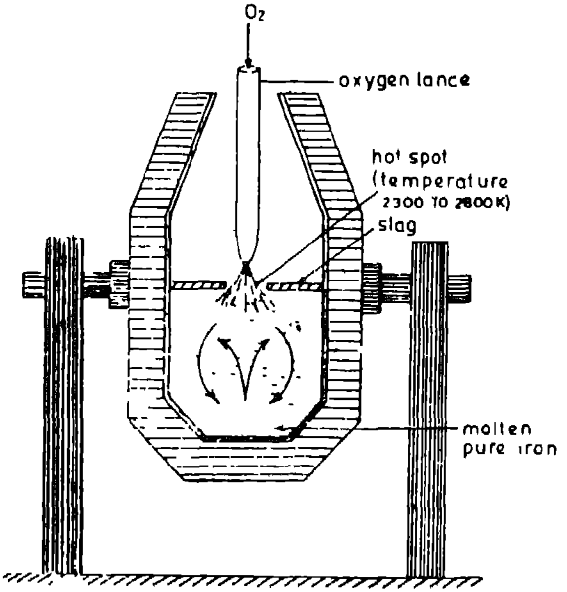

Fig. 14.2 L D. process of manufacturing steel (The oxygen is introduced at high pressure into the open end of the upright convertor containing the molten iron)

off with lime and MnO with silica forming fusible $CaSiO_3$ and $MnSiO_3$ respectively. The slag floats on surface of iron. The purified iron is denser than the impure one. Thus purified iron sinks to the bottom and the impure iron continues to rise to the top. Use of oxygen, instead of air, reduces the time requirement and has been found to be economical in practice.

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*Litz and Donawitz are the names of the towns in Austria where this process was developed and first used

14.7-2 HEAT TREATMENT OF STEEL

The hardness of steel depends on its carbon content and heat treatment. If a steel article is heated to redness and then suddenly cooled by plunging into water or oil, the treatment is called *quenching* Quenched steel becomes hard and brittle. If the quenched steel is reheated to a predetermined temperature and kept at it for a predetermined time, its mechanical properties become changed to a particular extent This treated steel is called *tempered steel* and the process is called *tempering* of steel. If steel be heated to a temperature well below red heat and is then cooled slowly, the process is called *annealing*. Annealed steel is soft

14.7-3 ALLOY STEELS

If to general steel with composition of iron and carbon, some other metal is added to modify its properties, we get an alloy steel Most important example of alloy steels is the *stainless steel*. It is called so because it is not stained or corroded by atmosphere, water, mild acids or mild alkalies There are a number of varieties of it The most common form is the eighteen-eight stainless steel which has 18% chromium and 8% nickel and the rest steel. In India we lack nickel and are rich in manganese and here a stainless form of steel has been developed which has manganese in place of nickel Stainless steel finds its major use for household utensils, shaving blades, watch cases, etc. Some information of this and other alloy steels are provided in Table 14.6.

TABLE 14·6

Some Alloy Steels

Steel	*Special components*	*Chief properties*	*Uses*
Nickel	Ni 3-5%	Hard, flexible, rust resistnant	For cables, armour plates
Stainless steel	Cr 18% Ni 18%	Does not rust or corrode	For household utensils, shaving blades, watch cases
Chrome-vanadium steel	Cr 1% V 0.15%	Tenacious and load bearing	For axles, springs and cogwheels

Steel	*Special components*	*Chief properties*	*Uses*
Manganese steel	Mn 12 to 15%	Exttremely hard and high melting	For rock crusher, burglar proof safes
Tungsten steel	W 14 to 20% Cr 3 to 8%	Very hard and strong	For cutting tools, springs
Invar	Ni 36%	Extremely low expansion on heating	For clock pendulums
Alnico	Al 12% Ni 20% Co 5%	Highly magnetic	For permanent magnets

14.7-4 COMPOUNDS OF IRON

Iron forms two series of compounds in which iron is respectively divalent (ferrous) and trivalent (ferric). Besides these, iron also forms complex compounds based on Fe (II) and Fe (III) states with co-ordination number upto 6 Yet another group of compounds fall under the group of *double salts*.

Ferrous compounds · Ferrous sulphate, $FeSO_4$, is the cheapest ferrous compound. It is commercially called green vitriol because of its green colour It crystallizes as $FeSO_4 \cdot 7H_2O$. It loses water of crystallization in steps to form hydrates with 5, 4 and 1 water molecules as well as the anhydrous salt. Anhydrous salt is used in medicines for supplementing iron in diet. Crystals effloresce in dry air. It decomposes on heating.

$$2FeSO_4 \longrightarrow 2FeO + 2SO_3$$

$$2FeO + SO_3 \longrightarrow Fe_2O_3 + SO_2$$

Ferrous salts act as reducing agents .

$$2FeSO_4 + H_2SO_4 + [O] \longrightarrow Fe_2(SO_4)_3 + H_2O$$

$$Fe^{2+} \longrightarrow Fe^{3+} + e^-$$

Ferrous sulphate in a solution can be estimated by titration with acidified solutions of $KMnO_4$ or $K_2Cr_2O_7$ With NO gas, $FeSO_4$ solution forms a dark brown compound $FeSO_4.NO$ This is decomposed on heating the solution. This reaction forms the basis of *brown ring test* for nitrates. To a solution of a nitrate, some ferrous sulphate solution is added and concentrated sulphuric acid is poured through the side of the tilted test tube. Due to its heaviness, the concentrated acid quickly sinks and forms a layer at the bottom. Some heat is developed at the boundry between the concentrated acid and the aqueous solution This helps in the reduction of NO_3^- ions to NO

$$3\,Fe^{2+} + NO_3^- + 4\,H^+ \xrightarrow{\text{warming}} 3\,Fe^{3+} + NO + 2\,H_2O$$

$$FeSO_4 + NO \longrightarrow FeSO_4\ NO \text{ (brown soluble compound)}$$

$$FeSO_4\ NO \xrightarrow{\text{Heat}} FeSO_4 + NO$$

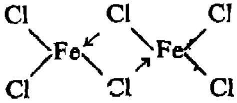
If the mixture is stirred, the heat of mixing of conc. H_2SO_4 raises the temperature sufficiently to destroy the brown compound When ferrous sulphate solution is mixed with an acidified solution of a nitrate whole solution becomes brown. Nitrous acid provides NO in all parts of the solution without needing any warming

Ferrous sulphate forms *double salts* with sulphates of monovalent cations The most important of these is ferrous ammonium sulphate $[FeSO_4\,(NH_4)_2SO_4\,6H_2O]$ or Mohr's salt. This salt is not so readily efflorescent as $FeSO_4\,7H_2O$ nor is it so readily oxidized by air. Hence it is used for making standard solutions of ferrous iron by direct weighing

Ferrous sulphate is used as cheap reducing agent, as a source of Fe $(OH)_2$ which is used as a mordant in dying and as a component of blue black inks.

Commercially important ferric salts are ferric chloride and ferric ammonium sulphate The latter is known as *ferric alum*, $Fe_2(SO_4)_3\,(NH_4)_2\,SO_4\,24H_2O$

Anhydrous ferric chloride can be prepared by passing chlorine gas over heated iron wire or scrap. When volatilised its vapour is a covalent compound with the molecular formula, Fe_2Cl_6.



It cannot be prepared from an aqueous solution due to easy hydrolysis of ferric chloride.

In contact with water Fe_2Cl_6 changes to the ionic forms and gets hydrolysed. Hydrolysis can be completed by boiling the solution.

$$Fe_2Cl_6(s) \xrightarrow{H_2O} 2Fe^{3+}(aq) + 6Cl^-(aq)$$

$$Fe^{3+}(aq) + 3H_2O(l) \longrightarrow Fe(OH)_3(s) + 3H^+(aq)$$

The aqueous solution shows acidic behaviour to litmus.

Ferric chloride is used in medicines as astringent, antiseptic in the form of tincture, liquor and iron glycerine. It provides $Fe(OH)_3$ which is an important mordant in dyeing. Block makers use a concentrated solution of ferric chloride for making etchings on metals like copper and silver. It is due to the oxidizing action of ferric ions.

$$^{+}(aq)+Cu(s) \longrightarrow Fe^{2+}(aq)+Cu^{2+}(aq)$$

$$Fe^{3+}(aq)+Ag(s) \longrightarrow Fe^{2+}(aq)+Ag^{+}(aq)$$

Potassium ferrocyanide, $K_4[Fe(CN)_6]$. It is a very stable complex compound. It reacts with ferric salts to form a deep blue precipitate of ferric ferrocyanide which is called *prussian blue*.

$$4Fe^{3+} + 3[Fe(CN)_6]^{4-} \longrightarrow \underset{\text{Ferric ferrocyanide}}{Fe_4[Fe(CN)_6]_3}$$

Potassium ferrocyanide can be oxidized to potassium ferricyanide by Cl_2, ozone or $KMnO_4$

$$2[Fe(CN)_6]^{4-} + Cl_2 \longrightarrow 2[Fe(CN)_6]^{3-} + 2Cl^-$$

14.7.5 PASSIVATION OF IRON

Powerful oxidizing agents like concentrated or fuming nitric acid form a thin, invisible and insoluble inert film of oxide on iron and some other metals. This is known as *passivation*. Passive iron does not react with acids or displace copper from copper salts. The passivity may be destroyed by scratching, scrubbing or hammering. Cobalt, nickel and chromium can also become passive

14.7.6 HAEMOGLOBIN

Iron is an essential element for our bodies. However, if all the iron in a man's body is separated we may get hardly a few grams of it. Most of this iron is present in the blood as haemoglobin which serves as oxygen carrier in the body. Iron in oxidation state II, is co-ordinated to four nitrogen atoms at the centre of a complex organic molecule. Oxygen is held loosely by the iron atom (structure of haemoglobin is given in Unit 20). If CO attaches to the central iron atom to form carboxy haemoglobin, blood loses its power of attaching oxygen and the person dies of suffocation. Same is true of cyanide poisoning or death by snake bite.

14.8 CORROSION

It is a process in which useful metals are lost as compounds, generally as oxides, due to chemical action with environments The metal surface becomes quite rough, indicating a non-uniform action. In case of iron, corrosion takes the form of *rusting* Rust is a hydrated form of ferric oxide, $Fe_2O_3 . xH_2O$ Moisture, oxygen and carbon dioxide present in air, are all collectively necessary for rusting. Rust formation is heaviest where an iron object is in contact with air Thus in water tanks made of iron, rust forms mostly near the top. Rust is a non-sticking compound It peals off exposing fresh iron surface for further rusting The chemical changes in rust formation may be indicated in the following steps and illustrated in Fig. 14.3a.

(i) $Fe \longrightarrow Fe^{2+} + 2e^-$

(ii) $H^+ + e^- \longrightarrow H$

(iii) $4H + O_2 \longrightarrow 2H_2O$

(iv) $2H \longrightarrow H_2$

(v) $4Fe^{2+} + O_2 + 4H_2O \longrightarrow 2Fe_2O_3 + 8H^-$

(vi) $Fe_2O_3 + xH_2O \longrightarrow Fe_2O_3 . xH_2O$

In the chain of these steps the first step will not take place unless some electron acceptor is available nearby H^+ ions from water and from a solution of carbon dioxide in water, thus become necessary for corrosion Oxygen is necessary for removal of atomic hydrogen and for oxidizing the ferrous iron to the final ferric state

Rusting and most other corrosions are *electro-chemical processes.* They occur when a metal finds in its neighbour some species to which it can pass on its electrons. They are aided by impurities and strains at metal surfaces.

14.8-1 PREVENTION OF CORROSION

A number of techniques are used for preventing corrosion of metals. These may be illustrated by taking examples of processes used for preventing rusting of iron. (Fig. 14 3) (b), (c) and (d) illustrate different method of protection.

(i) *Barrier protection* : A barrier film is made between iron and atmospheric air This can be an impenetrable film of an oil, a paint or another metal which itself is not corroded by air Such metals are chromium, nickel, tin and copper. Thus a housewife keeps iron article painted with oil: Motor cars and even big ships made from iron sheets are kept completely painted. Iron articles are electroplated with chromium and nickel not only for lustrous decoration but also for protection. If there are any cracks or scratches in the protective film, rusting of iron starts and spreads below the film. The film peals off and the article becomes exposed.

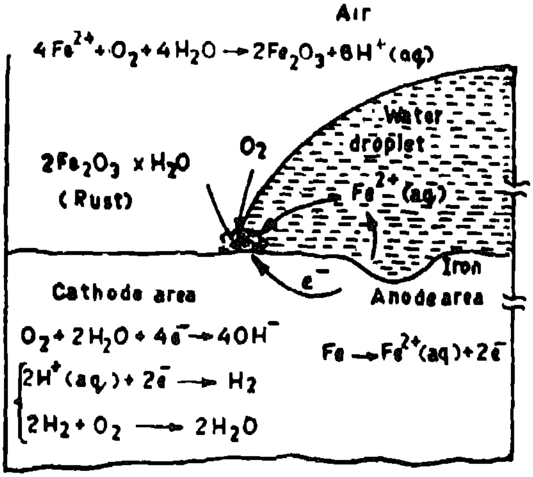

Air
$4Fe^{2+} + O_2 + 4H_2O \rightarrow 2Fe_2O_3 + 8H^+(aq)$
Water droplet
O_2
$2Fe_2O_3 \cdot xH_2O$
(Rust)
$Fe^{2+}(aq)$
e^-
Iron
Cathode area
Anode area
$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$
$2H^+(aq) + 2e^- \rightarrow H_2$
$2H_2 + O_2 \rightarrow 2H_2O$
$Fe \rightarrow Fe^{2+}(aq) + 2e^-$

Fig. 14.3 (a) Corrosion of iron in contact with water and air

(ii) *Sacrificial protection*. In this method, iron surface is covered with a layer of a metal more active than iron. This prevents loss of electrons from iron The more active metal loses electrons preferentially and goes into ionic state The covering metal gets consumed in course of time but so long as it is available, even the nearby

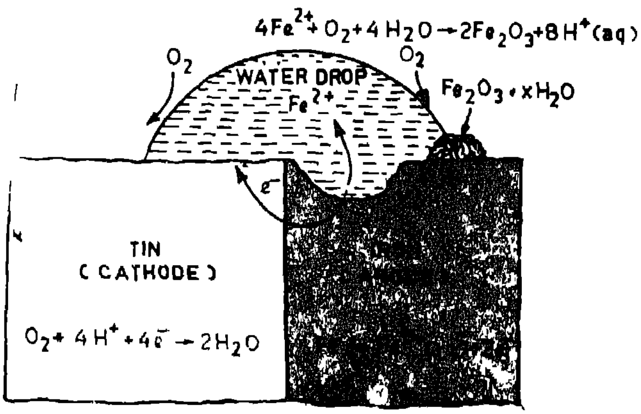

$4Fe^{2+} + O_2 + 4H_2O \rightarrow 2Fe_2O_3 + 8H^+(aq)$
O_2
O_2
WATER DROP
Fe^{2+}
$Fe_2O_3 \cdot xH_2O$
e^-
TIN
(CATHODE)
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$

Fig. 14.3 (b) Barrier protection with a film of tin. Film will be effective so long it is intact. Rusting occurs at the exposed iron surface.

exposed surfaces of iron do not react. Scratches in protective films of this type produce no ill effects. The metal most often used in this way for covering iron surfaces is zinc. The process of covering iron with zinc is called *galvanization.* Galvanized iron sheets maintain their lustre due to the formation of a protective invisible thin layer of basic zinc carbonate, $ZnCO_3{\cdot}Zn(OH)_2$, on the zinc film by moisture, oxygen and carbon dioxide in air. Zinc, magnesium and aluminium powders can also be applied as protective layers, mixed with paints.

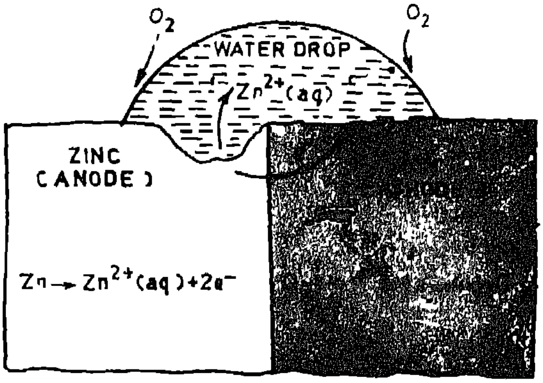


Fig. 14.3 (c) Sacrificial protection with a film of zinc Rusting does not occur even when iron surface is exposed

(iii) *Electrical protection:* The exposed part of iron surface in contact with water can also be protected by imparting a positive electrical potential to it. This checks its tendency to lose electrons. Cathodes of magnesium or zinc can be fixed to the surface of iron or burried in subsoil water nearby.

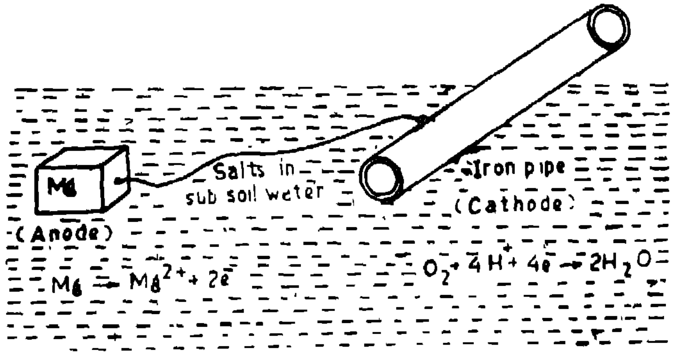

Mg
(Anode)
Salts in sub soil water
Iron pipe
(Cathode)
$Mg \rightarrow Mg^{2+} + 2e$
$O_2 + 4H^+ + 4e \rightarrow 2H_2O$

Fig. 14 3 (d) Electrical protection of iron pipes burried underground

(iv) *Using anti-rust solutions:* These are alkaline phosphate and alkaline chromate solutions. The alkaline nature of these solutions prevents availability of H^+ ions Phosphate tends to deposit a protective insoluble sticking film of iron phosphate Anti-rust solutions are used in car radiators to prevent rusting of iron parts of engine

14.9 METALS OF COPPER GROUP

Metals of interest in this group are copper (Cu from cuprum), silver (Ag from argentum) and gold (Au from aurum) These are collectively known as coinage metals though this use has been given up by most of the countries including India. Our coins are now based on aluminium and nickel. All metals of copper group occur in nature in a free state as well as in the form of compounds. Copper is extracted from sulphide and oxide ores. Native silver is now relatively rare and most of the silver is obtained from silver chloride (horn silver) and silver sulphide (argentite or silver glance) as ores Gold is still mostly mined in native state or is recovered from anode mud obtained in the electro-refining of other metals like copper and nickel Compound form of gold found in nature is gold telluride ($AuTe_3$).

Metallurgies of these metals have been discussed earlier (Unit 13)

14 9-1 PROPERTIES OF COPPER, SILVER AND GOLD

All the three metals are less reactive than hydrogen and do not displace it from acids, water or alkalies. The general reactivities of these metals are in the order Cu>Ag>Au. Gold is sufficiently unreactive to be treated as a noble metal. Gold does not react with even oxidizing acids which can react with and dissolve copper and silver.

(i) *Action of air* · Ordinary air has no action on any of these metals but on being heated in air, copper alone reacts to form an oxide.

$$2\,Cu + O_2 \xrightarrow{\text{below 1400K}} 2\,CuO$$

$$4\,Cu + O_2 \xrightarrow{\text{above 1400K}} 2\,Cu_2O$$

(ii) *Action of water :* There is no action as such. At white heat temperature copper decomposes steam.

$$2\,Cu + H_2O \rightleftharpoons Cu_2O + H_2$$

(iii) *Action of acids* · Hydracids in general and dilute H_2SO_4 have no action in absence of dissolved oxygen. Copper reacts with dilute H_2SO_4 and hydracids when oxygen is available.

$$2\ Cu + 2H_2SO_4 + O_2 \longrightarrow 2\ CuSO_4 + 2H_2O$$

$$2\ Cu + 4\ HCl + O_2 \longrightarrow 2\ CuCl_2 + 2H_2O$$

Silver and gold do not react even under these conditions. Concentrated hot sulphuric acid dissolves copper and silver but not gold.

$$H_2SO_4 \equiv H_2O + SO_2 + [O]$$

$$Cu + [O] + H_2SO_4 \xrightarrow{\text{heat}} CuSO_4 + H_2O$$

$$2\ Ag + [O] + H_2SO \xrightarrow{\text{heat}} Ag_2SO_4 + H_2O$$

Dilute nitric acid reacts with copper and silver to give nitric oxide and the concentrated nitric acid reacts giving nitrogen dioxide. Gold dissolves in aqua regia ($3HCl+HNO_3$).

$$2HNO_3\ (\text{dilute}) \equiv H_2O + 2NO + 3\ [O]$$

$$2HNO_3\ (\text{conc.}) \equiv H_2O + 2NO_2 + [O]$$

$$Cu + [O] + 2HNO_3 \longrightarrow Cu\ (NO_3)_2 + H_2O$$

$$2Ag + [O] + 2HNO_3 \longrightarrow 2\ AgNO_3 + H_2O$$

$$3HCl + HNO_3 \equiv NOCl + 2H_2O + 2Cl$$

$$Au + 3Cl \longrightarrow AuCl_3$$

$$Au + 3Cl + HCl \longrightarrow HAuCl_4$$

(iv) *Action of alkalies :* Alkalies do not react with these metals and may be fused in crucibles made of copper, silver or gold.

(v) *Action of hydrogen sulphide* Hydrogen sulphide as such or its traces present in air or sulphur containing foods can react with copper and silver to form the respective sulphides. This action by H_2S is induced by the greater stability of the sulphides of metals than of hydrogen sulphide

(vi) *Displacement reactions* · Copper can displace silver and gold from solutions of their salts. Silver can displace gold, but gold being the least reactive does not take part in displacement reactions. (A photograph takes up colour of gold when treated with a solution of gold chloride but it does not change its colour when dipped into a solution of copper chloride. Explain?).

(vii) *Action of ammonia* · Copper dissolves in an aqueous solution of ammonia in presence of air forming a deep blue coloured solution.

$$2Cu + 8\ NH_3 + 2H_2 + O_2 \longrightarrow 2\ [Cu\ (NH_3)_4]^{2+}\ (OH^-)_2$$

Silver and gold remain unaffected.

(viii) *Action of ozone* · Ozone oxidizes copper and silver surfaces but does not tarnish gold

$$Cu + O_3 \longrightarrow CuO + O_2$$

$$2Ag + O_3 \longrightarrow Ag_2O + O_2$$

$$Ag_2O + O_3 \longrightarrow \underset{\text{(black)}}{2Ag} + 2O_2$$

$$2O_3 + (Au) \longrightarrow 3O_2 + (Au)$$

14.9.2 USES OF COPPER GROUP METALS

Copper is mainly used in electrical units as wire. This is due to good electrical conductance of pure copper. Copper forms important alloys (Table 14.7) which are hard, tenacious, corrosion resistant, gold-like in colour and good conductors of heat. Copper is used for covering more active metals as copper gets covered with a sticky thin layer of an oxide which prevents further damage by weather conditions.

TABLE 14.7

Alloys of Copper

Alloy	*Percentages of components*	*Use*
Brass	Cu = 60 Zn = 40	Utensils and cartridge caps
Bronze	Cu = 90 Sn = 10	Control valves, statues
Aluminium bronze	Cu = 90 Al = 10	Golden powder for paints, cheap jewellery
Phosphor bronze	Cu = 95 Sn = 4.8 P = 0.2	Springs and suspension filaments in electrical instruments
Bell metal	Cu = 80 Sn = 20	Bells
Gun metal	Cu = 88 Sn = 10 Zn = 2	Gears and bearings
German silver	Cu = 25—50 Zn = 25—35 Ni = 10—35	Utensils, resistance wire

Silver is used in jewellery and as wealth It is used for sparking plugs as it does not get oxidized on being heated in air Silver salts are used in photography and in electroplating with silver

The main use of gold is as an article of wealth and in jewellery Gold suspensions are used in galvanometers as it can be drawn into very fine wires and is a very good conductor of electricity. From long time past gold foil has been used for covering temple domes as gold is not corroded by atmospheric conditions

Gold is sold as stamped pieces called gold biscuits. Purity of gold is quoted on the *carat* scale Pure gold is 24 carat. 22 carat gold often used for jewellery in India is 22 parts gold and 2 parts the alloying metal, silver or copper

14.10 COMPOUNDS OF COPPER

Copper forms two series of compounds with oxidation states +1 and 2 cuprous and cupric respectively Cuprous compounds are stable only when insoluble Cuprous ions in solution readily disproportionate to copper and cupric ions

$$2\,Cu^{+} \longrightarrow Cu + Cu^{2+}$$

Cuprous compounds can be stabilized by complex formation with high concentrations of halides, cyanides and ammonia

$$CuCl + 3\,Cl^{-} \longrightarrow [CuCl_4]^{3-}$$

$$CuCN + CN^{-} \longrightarrow [Cu(CN)_2]^{-}$$

$$CuCl + 2\,NH_3 \longrightarrow [Cu(NH_3)_2]\,Cl$$

Cuprous iodide is precipitated when an iodide solution is mixed with a solution of cupric salt (e g. copper sulphate).

$$2\,Cu^{2+} + 4\,I^{-} \longrightarrow 2\,CuI + I_2$$

The liberation of iodine is quantitative and can be used for estimating cupric salt in a solution.

The most common compound of copper is copper sulphate It is known commercially as *blue vitriol* ($CuSO_4 . 5\,H_2O$). The penta hydrate crystals are quite stable but they effloresce in very dry air. These crystals on dehydration give $CuSO_4\ 3H_2O$, $CuSO_4.H_2O$ and the anhydrous $CuSO_4$. The anhydrous copper sulphate is white in colour. It is used as a sensitive test for moisture in contact with which it turns blue. On strong heating copper sulphate decomposes.

$$CuSO_4 \xrightarrow{\text{heat}} CuO + SO_3$$

In aqueous solutions cupric ions give a blue colour due to $[Cu(H_2O)_4]^{2+}$ ions. The deep blue colour given by cupric salt solution with ammonia is due to the formation of $[Cu(NH_3)_4]^{2+}$ ions

Verdigris is basic copper acetate $Cu(CH_3COO)_2.Cu(OH)_2$. The fungicide, *Bordeaux mixture*, is a mixture of copper sulphate and milk of lime

14.11 COMPOUNDS OF SILVER

Most common compound of silver is *silver nitrate* ($AgNO_3$). It is also sometimes called *lunar caustic*. It is obtained as a **by-product** from gold refineries where impure gold is purified by the *parting* process. Even impure gold does not react with nitric acid. It is first melted with silver and then the gold-silver alloy is heated with nitric acid in aluminium vessels. Silver and other impurities like copper are dissolved leaving behind gold in a finely divided state. The powder is melted to get buttons of gold. In this form gold is commercially known as 'Vitur'. The silver nitrate may be crystallized or converted back to silver by treatment with copper turnings.

Commercial silver nitrate crystals have an impurity of copper nitrate. If these crystals are carefully heated, copper nitrate, being more easily decomposable, forms CuO. The latter being insoluble can be separated from the soluble $AgNO_3$.

Silver nitrate decomposes on heating:

$$2\,AgNO_3 \xrightarrow{\text{low heat}} 2\,AgNO_2 + O_2$$

$$2\,AgNO_3 \xrightarrow{\text{above 1 000K}} 2\,Ag + 2NO_2 + O_2$$

Silver nitrate solution may be reduced to give a silver mirror when an alkaline solution of silver nitrate is reduced with organic reducing agents like formaldehyde or sodium potassium tartarate.

Silver nitrate solution reacts with a number of anions to give precipitates. These reactions are used as tests for those anions.

$Ag^+ + Cl^- \longrightarrow AgCl$ (white, soluble in NH_4OH)

$Ag^+ + Br^- \longrightarrow AgBr$ (pale yellow, slightly soluble in NH_4OH)

$Ag^+ + I^- \longrightarrow AgI$ (yellow, insoluble in NH_4OH)

$2\,Ag^+ + CrO_4^{2-} \longrightarrow Ag_2CrO_4$ (brick red)

$3\,Ag^+ + PO_4^{3-} \longrightarrow Ag_3PO_4$ (yellow)

$2\,Ag^+ + S^{2-} \longrightarrow Ag_2S$ (black)

Silver nitrate being the cheapest salt of silver, is the starting material for preparing other silver compounds. It is used in silver plating baths (mixed with KCN), for making silver mirrors, as marking ink for clothes, as a germicide in medicine, as an application in eye diseases, and as a volumetric reagent for estimating halides.

Amongst other silver compounds to mention are *silver halides.* Silver fluoride is soluble in water but the other halides are not. The insoluble silver halides find use in photography (see Section 14.12) They are all sensitive to light and are dissolved by a solution of sodium thiosulphate They can be reduced to metalic silver by alkaline solutions of hydroquinone. They are converted to metal on being fused with sodium carbonate or on treatment with zinc dust.

$$AgBr + 2\ S_2O_3^{2-} \longrightarrow [Ag(S_2O_3)_2]^{3-} + Br^-$$

$$\underset{\text{hydroquinone}}{C_6H_4(OH)_2} + 2\ AgBr \xrightarrow{\text{alkali}} \underset{\text{quinone}}{C_6H_4O_2} + 2\ Ag + 2\ HBr$$

$$4\ AgCl + 2\ Na_2CO_3 \xrightarrow{\text{heat}} 4\ Ag + 4\ NaCl + 2\ CO_2 + O_2$$

$$2\ AgCl + Zn \longrightarrow 2\ Ag + ZnCl_2$$

14.12 PHOTOGRAPHY

The process of producing pictures by using light images is called *photography.* It is based on sensitiveness of silver halides, particularly AgBr, to light. The different steps in obtaining a photograph are described below

(1) **Preparation of sensitive plate or film :** An emulsion of AgBr in gelatin solution is uniformly coated on a transparent film or glass plate. This is done in a dark room.

(2) **Exposure to light image :** This is done by loading the sensitive film in a camera. On a momentary opening of the shutter, image of the object falls on the sensitive plate. An invisible change occurs in parts of emulsion on which light falls.

$$Br^- + \text{Photon} \longrightarrow e^- + .Br\ \text{(absorbed on gelatin)}$$

$$Ag^+ + e^- \longrightarrow Ag$$

The number of silver atoms thus formed are proportional to the number of photons received by the plate, but they are too few to be visible The image on the film remains dormant or latent. However, the silver atoms formed in this step catalyze the development step.

(3) **Development of image :** The exposed film is passed through a reducing bath containing an alkaline solution of quinol (hydroquinone), metal or amidol. More silver bromide gets reduced to give black silver in areas exposed to light in propor-

tion to the intensity of light Only just enough time is allowed for the action in the bath to get the desired visibility of image As there will be unreacted AgBr on the film, this step is carried out in the dark to prevent a general blackening of the picture.

$$2AgBr + C_6H_4(OH)_2 \xrightarrow{(Ag)+OH^-} 2Ag + 2HBr + C_6H_4O_2$$

The image is made visible in this step However, the brightest parts of the picture are shown as the darkest in this picture. For example, the face of a person will look dark and his hair will look grey On account of the reversal of shades, the developed picture is called the *negative*

(4) **Fixing of the negative picture** . The film is next passed through a bath of sodium thiosulphate solution. Photographers call this substance *hypo*. This step is also carried out in darkness. Here, the AgBr still remaining on the film is dissolved by chemical action with the thiosulphate.

$$AgBr + 2S_2O_3^{2-} \longrightarrow [Ag(S_2O_3)_2]^{3-} + Br^-$$

Since the film will not have any more unreacted AgBr, it will no longer be necessary to keep it in darkness.

(5) **Printing out of positive picture** : The negative film is put in contact with printing out bromide paper or another sensitive film Light is flashed over it through the negative for a few moments. The exposed paper or film is again passed through the development and fixation steps to get the positive image which tallies with the object in shades. This gives a *black and white picture*.

(6) **Negative reversal** : It is an alternative method of getting positive pictures. This is carried out before the fixation step. The developed negative picture is treated with an acidic oxidizing agent which dissolves out the black deposit of silver particles without affecting the unconverted AgBr So the film will have AgBr in varying density over the film according to the shades of the negative. Next the film is directly exposed to light for a short time. It is then developed and fixed in the dark. The result is a positive picture on the original film. It is a transparent picture. This process is useful for making *slides*.

(7) **Toning** : In this step the appearance of a photograph is changed by partial replacement of silver in the photograph. The commonly adopted procedures are :

(i) *Gold toning* : A dilute solution of sodium tetrachloroaurate (III) is applied to the surface of the photograph. Some of the silver in the surface layer is replaced by gold and the picture takes up a golden hue.

$$Na[AuCl_4] + 3Ag \longrightarrow NaCl + 3AgCl + Au$$

(ii) *Platinum toning* A dilute solution of potassium hexachloroplatinate (IV) is applied to the photograph surface Replacement of some of the silver by platinum gives a bright grey tone to the photograph.

$$K_2[PtCl_6] + 4Ag \longrightarrow 2KCl + 4AgCl + Pt$$

(iii) *Sulphur toning* · On treating a photograph with a colloidal solution of sulphur some silver is converted to Ag_2S and the picture gets a sepia tone.

(iv) *Blue toning* · When a photograph is treated with a mixed solution of $FeCl_3$ and $K_3[Fe(CN)_6]$, some of the silver gets replaced by the blue coloured ferro-ferricyanide, $Fe_3[Fe(CN)_6]_2$.

$$Ag + Fe^{3+} + Cl^- \longrightarrow AgCl + Fe^{2+}$$

$$3Fe^{2+} + 2\,[Fe(CN)_6]^{3-} \longrightarrow Fe_3[Fe(CN)_6]_2$$

(v) *Dye toning* A black and white photograph may be dyed or painted to give a more pleasant appearance Gelatin easily catches colouring materials

14 13 MIRRORS

Mirrors are obtained by depositing smooth metal surfaces on evenly ground glass plates. Following steps are involved in making a mirror

(1) *Preparation of glass plate :* Glass plates sent out by rolling factories are not quite even and smooth For making a mirror the plate is set horizontally on a flat surface and ground and polished with fine grinding powder It is thoroughly cleaned with some detergent and washed with water. Its boundaries are edged and the plate is set for leveling in a warm place.

(2) *Preparation of silvering solution :* 20g of $AgNO_3$ is dissolved in about 150 ml of water. Ammonia solution is added till the brown precipitate first formed is just redissolved by stirring. The solution is made upto 300 ml. It is mixed immediately before use with a slow acting reducing agent like sodium potassium tartarate (Rochelle salt), glucose or formaldehyde

(3) *Mirroring :* The mixed silvering solution is poured over the plate to cover it evenly and allowed to stand for long enough to give a desired thickness of silver film over the glass plate. The solution is then poured off and the plate is washed.

(4) *Backing :* Since the silver film is very thin and can be easily scratched, it is protected by electroplating it with sufficient copper. For cheap mirrors a coating of red lead paint is applied instead of depositing a layer of copper.

This process gives mirrors with a back polish Front polish mirrors are obtained by grinding smooth the front surfaces of white metal plates.

14.14 METALS AND COMPOUNDS OF ZINC GROUP

Zinc, cadmium and mercury are the three metals belonging to this group. They have the electronic configuration of $(n-1)d^{10}, ns^2$ Thus they do not have any incompletely filled or empty inner shell orbitals The major mode of their chemical combination involves the ns^2 electrons only These electrons can be given over to electron accepting atoms or groups This feature makes zinc and cadmium metals very similar to magnesium although considerably less reactive. Their activities decrease in the order $Hg < Cd < Zn$. Mercury tends to show the property of catenation and forms Hg_2^{2+} ions.

In air zinc and cadmium get covered with a protective layer of oxide They burn to form the oxides, on being heated in air Mercury forms a red oxide (HgO) near its boiling point (573K). On being heated further (673K), mercury oxide breaks up into the metal and oxygen. These metals also combine with the halogens and sulphur. Zinc and cadmium react with dilute acids to displace hydrogen Mercury reacts only with oxidizing acids. Zinc alone reacts with hot alkalies forming zincate ions.

$$Zn + 2\ NaOH \longrightarrow Na_2ZnO_2 + H_2$$

These metals have a weak metal bonding. Consequently they are quite volatile as metals. Mercury is liquid at ordinary temperatures Mercury vapour is highly toxic and relative inertness of mercury makes it a cumulative poison. Mercury is slightly soluble in water. This enhances danger from mercury.

Soluble mercury compounds are highly poisonous. The mercurous compounds like calomel (Hg_2Cl_2) are not poisonous mainly because of extreme insolubility. The insoluble compounds of mercury and zinc act as germicides Calomel and zincite (ZnO) and calamine ($ZnCO_3$) are used in medicinal ointments Mercury is an opaque liquid with a density of about 13.6 g/cm^3. This makes it useful as a thermometric and barometric liquid.

Galvanization is a process of covering iron sheets with zinc by passing cleaned plates through molten zinc.

Alloys of mercury with other metals are called *amalgams*. These may be in liquid or solid form. An amalgam of sodium is less reactive than pure sodium (dilution effect), while an amalgam of aluminium is far more reactive than aluminium (loss of protective layer of oxide).

Lithopone is white pigment consisting of ZnS and $BaSO_4$. Zinc phosphate is used as a dental cement and zinc chloride solution is used as flux in soldering.

Cadmium sulphide is an important yellow pigment.

Mercury sulphide can be had in black and red forms. The latter is called *vermilion* and is an article of ladies' cosmetics. Makaradhwaj, an Ayurvedic medicine, is sublimed mercury sulphide. Mercury readily reacts with sulphur when the two are rubbed together. Sulphur powder is sprinkled over spilt mercury to prevent poisoning by mercury vapour.

Scarlet red mercuric iodide, HgI_2, dissolves in KI solution to form a colourless solution of $K_2[HgI_4]$. An alkaline solution of potassium tetraiodomercurate (II), $K_2[HgI_4]$ is called *Nessler's reagent*. This reagent gives a brown colour or precipitate with ammonia or ammonium salts. This is a very sensitive test.

Mercuric cyanate, $Hg(CNO)_2$, is an explosive known as *fulminate of mercury*.

Cheapest mercury compound is mercuric chloride, $HgCl_2$. It can be easily sublimed and is called *corrosive sublimate*.

EXCERCISES

14.1 What are transition elements ? Which of the *d*-block elements are not regarded as transition elements ?

14.2 In what way the electronic configurations of transition elements are different from those of representative elements ?

14.3 Transition elements show a variation in oxidation states. What is the reason for it and how is this variation different from that shown by the *p*-block elements ?

14.4 In the transition series starting with lanthanum (atomic number, 57), the next element hafnium has an atomic number of 72. Why do we observe this jump in atomic number ?

14.5 How do you explain the anomalous electronic configurations of Cr ($4s^1 3d^5$) and Cu ($4s^1 3d^{10}$)?

14.6 The transition group metals should be more reactive than hydrogen according to their electrode potentials. How is it then that most of these do not displace hydrogen from dilute acids ?

14.7 Why do transition elements show similarities along the horizontal period as well as down a vertical group ?

14.8 How is it that several transition metals act as catalysts ? Give some examples of reactions catalyzed by them.

14.9 Define and illustrate the terms complex, ligand, polydentate, co-ordination number, chelation.

14.10 Transition metals easily form intermetallic alloys. What property of these metals would you consider to be responsible for it ?

14.11 How do you account for paramagnetism and colours observed for compounds of transition elements ?

14.12 Describe applications of complex formation by ions of transition metals.

14.13 What are masking agents ?

14.14 How is it that in alkaline solutions we have chromates and in acidic solutions dichromates ?

14.15 Write equations for the oxidation of acidified solutions of ferrous sulphate, potassium iodide and sulphur dioxide by potassium dichromate solution.

14.16 Write a note on chemical valcano.

14.17 Chrome alum is prepared by passing SO_2 into a solution of potassium dichromate. Write equations for the reactions involved

14.18 A serious accident occurred in a chemical laboratory when a student tried to dissolve $KMnO_4$ in conc. H_2SO_4 instead of dilute H_2SO_4. What went wrong ?

14.19 Describe how steel may be obtained from cast iron ?

14.20 What are alloy steels ? Give three examples.

14.21 Describe the processes known as quenching, tempering and annealing.

14.22 Describe the ring test for nitrates.

14.23 Give the chemical names and uses of (i) Mohr's salt, and (ii) ferric alum.

14.24 (a) What is meant by passivation ? How may we make iron passive and how can passive iron be made reactive ? (b) An oxide film acts as a protection for aluminium but an oxide film cannot protect iron Explain.

14.25 (a) Write an essay on corrosion and its prevention. (b) Formulate the corrosion when iron washers are used in contact with (i) copper plates (ii) aluminium plates.

14.26 For removal of oxygen from commercial nitrogen, it is passed through copper chips kept in ammonia solution Explain.

14.27 How may we make copper sulphate from copper turnings and silver nitrate from an alloy of silver and copper ?

14.28 How may we protect :

(a) metal domes of temples against weathering,
(b) silver jewellery against tarnishing, and
(c) iron sheets against rusting ?

14.29 Describe the action of heat on
(i) ferrous sulphate, (ii) blue vitriol, (iii) mercuric oxide.

14.30 Describe the chemical changes involved in

(i) dissolving silver sulphide in KCN solution.
(ii) dissolving silver chloride in ammonia solution.
(iii) dissolving silver bromide in hypo solution.

14.31 Write essays on (i) photography, and (ii) mirror making

14.32 (i) Colamine, (ii) Calomel, (iii) Verdigris, (iv) Corrosive sublimate, (v) Vermilion, (vi) Nessler's reagent ?

14.33 Explain . A photograph when placed in a solution of gold chloride takes up a golden tinge but when placed in a solution of copper sulphate, nothing happens to it.

UNIT 15

Inner Transition or *f*-Block Elements

We have already studied about representative elements, and *d*-block elements. In the present Unit we shall study about *f*-block elements.

15.1 *f*-BLOCK ELEMENTS

There are two series of elements which are generated by the filling of characteristic electrons in the 4*f*-and 5*f*-orbitals. The 4*f*-group of elements following lanthanum, La (atomic number : 57) is called the *lanthanide series.* There are seven *f*-type orbitals in an energy shell; these can take up upto 14 electrons in them. Thus there are 14 elements in the lanthanide series starting with cerium, Ce (atomic number : 58) and ending with lutetium, Lu (atomic number : 71). These 14 elements have an interesting history of their discovery. Because of closely similar properties of these elements and their compounds, their separation and identification proved a very difficult task. The first stage in their separation was to get them as oxides. Most of these oxides, being available only in small quantities, have been called *rare earths* and the elements themselves have been called *rare earth elements.**

The 5*f* series of elements follows the element actinium, Ac (atomic number : 89). These are collectively called the *actinides.* They include the elements from thorium, Th (atomic number : 90) to lawrencium, Lr (atomic number ; 103). There are again 14 elements as expected. Included in this series is the element uranium U (atomic number : 92) which is the last element to occur in nature. The rest of the elements which have been made in the laboratories, are said to be man-made elements. They and the other elements beyond lawrencium already made or to be made later, are also known as *transuranic* or *transuranium elements.*

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* Though this class name has persisted in use, later evidence on occurrence of several of the lanthanide elements has shown that they are not so rare and several other elements are much rarer.

The actinides and the other transuranic elements are all radioactive.

15.2 THE LANTHANIDES

The chemistry of separation of naturally occurring lanthanides is too complex to be discussed in the present course. Here, we shall touch upon only a few of their properties.

The energies of the *d*-orbitals and the next inner shell *f*-orbitals are closely similar and the order of filling the *f*-orbitals shows frequent irregularities. Table 15 1 shows the electronic configurations of the lanthanides. Normal filling of *4f-orbitals is found only for atomic numbers 58, 64 and 71.*

TABLE 15.1

Ground State Electronic Configurations of 4*f*—Elements

Element	*Atomic number*	*Electronic configuration*
La	57	$5d^1 6s^2$
Ce	58	$4f^1 5d^1 6s^5$
Pr	59	$4f^3 5d^0 6s^2$
Nd	60	$4f^4 5d^0 6s^2$
Pm	61	$4f^5\ 5d^0 5s^2$
Sm	62	$4f^6 5d^0 6s^2$
Eu	63	$4f^7 5d^0 6s^2$
Gd	64	$4f^7 5d^1 6s^2$
Tb	65	$4f^9 5d^0 6s^2$
Dy	66	$4f^{10} 5d^0 6s^2$
Ho	67	$4f^{11} 5d^0 6s^2$
Er	68	$4f^{12} 5d^0 6s^2$
Tm	69	$4f^{13} 5d^0 6s^2$
Yb	70	$4f^{14} 5d^0 6s^2$
Lu	71	$4f^{14} 5a^1 6s^2$

Lanthanides are more reactive than the *d*-block elements. They react with water at room temperature to displace hydrogen. They rapidly combine with halogens, oxygen, sulphur and hydrogen in the temperature range 425 to 575K. They act as strong reducing agents for oxides of other metal. Cerium is used as a scavenger of oxygen and sulphur in several metals. Lanthanides use their f-orbital electrons for chemical bonding to a much less extent than the transition elements use their d-orbital electrons. Thus lanthanides show very little variation in oxidation states. The most common oxidation state observed with lanthanides is of +3. There are a few cases of +2 and +4 oxidation states.

The fluorides, hydroxides, oxides, carbonates, phosphates, chromates, and oxalates of lanthanides are largely insoluble. Solubilities of sulphates vary between extremes. The halides other than fluorides, nitrates and acetates are water soluble.

15.3 LANTHANIDE CONTRACTION

As we descend in a group of the Periodic Table, atomic sizes normally increase. This is due to the introduction of extra shells of electrons between the successive periods. On moving across a period from the left to the right, atomic sizes decrease. This is attributed to increasing attraction on the outermost shell electrons as the nuclear charge increases from element to element As an illustration we find that covalent atomic radii (radii of atoms in covalently formed molecules—an available property for comparing atomic sizes) increase from 1 23 Å for Li to 2.35 Å for Cs in the alkali metals and from 0 72 Å for F to 1.33 Å for I in the halogens They decrease from 1.23 Å for Li to 0.72 Å for F in the second period and similarly in the third period.

In the development of a period of elements notable change from element to element is the addition of one more proton (and some more neutrons) to the nucleus and one more electron outside the nucleus. In the first three periods the additional electron enters the s or p orbitals of the ultimate or outermost shell Since the rate of decrease in atomic sizes in the second and the third periods is rapid, it is persumed that the nuclear charge is able to exert its full attraction on the ultimate shell electrons. The electrons present in the incompletely filled s or p orbitals of the ultimate shell do not screen or shield each other against attraction of the nucleus.

In the development of the fourth and the fifth periods of elements, electrons also start filling the d-orbitals of the penultimate shell to give rise to the first and the second series of transition elements. As at this stage the additional electron gets added to an inner shell, it could be expected that it would have completely neutralized the effect of increase in nuclear charge due to the addition of a proton. Then there would have been no change in atomic sizes which are determined by the position of electrons in the ultimate shell. However, in these elements the decrease in atomic sizes with increase in nuclear charge from one element to the next is not quite significant, though not at the same rate as in the s-and p-block elements of the second and the third periods This shows that the electrons in the d-orbitals of the penultimat shell do not permit the nucleus to exert its full force of attraction on the electrons i the ultimate shell. The electrons in the d-orbitals possess some *shielding* or *screenin* influence on the nucleus, though it is incomplete. In any case the shielding influenc of electrons in d-orbitals is more than that of electrons in the s-and p-orbitals. Wit the filling in of 10 electrons in the d-orbitals from Sc (At no. 21) to Zn (At. no. 30 the covalent atomic radii decrease form 1 44Å to 1.25Å and from Y (At. no. 39) t Cd (At no 48) the decrease is from 1.62Å to 1.41Å. The somewhat reduced rate o contraction in atomic sizes for the transition elements is called *transition contraction* As a consequence of the introduction of the transition series between the p-bloc elements of the third and the fourth periods, the increase in atomic sizes in the group is somewhat less marked than in case of similar elements of the second and the thir periods.

In the development of the sixth period of elements, filling of electrons als commences in the $4f$-orbitals of the antepenultimate shell. We find that the decreas in atomic sizes from element to element in the first inner transition series o f-block elements (lanthanides) is much smaller than even in the d-block element of the fourth and the fifth periods. From Ce (At. no. 58) to Lu (At.no.71) covalen atomic radii decrease from 1.65 Å to 1 56 Å. For an increase in atomic number o fourteen, the total decrease in covalent atomic radii is of only 0.09 Å. This rathe small decrease in atomic sizes of elements in the lanthanides indicates that th shielding influence of electrons in the antepenultimate shell f-orbital is much stronge than that of even the electrons in the d-orbitals of the penultimate shell. This ver small rate of decrease in atomic sizes in the lanthanide elements has been name as *lanthanide contraction* It has a prominent influence on the chemistry of no only the lanthanides themselves but also of the elements which follow then in the transition series of the sixth period. Thus, Hf (At no.72) has a covalen atomic radius of 1 44Å, Zr (At. no. 40), an element immediately above Hf i the group, has a covalent atomic radius of 1.45 Å. This is an unusual happening Normal thing to occur in any group is an increase in atomic size. This unusua relationship in atomic sizes persists for elements which follow Hf in the sixth period Lanthanide contraction almost balances the expected increase in atomic sizes o some group elements between the fifth and the sixth periods of the Periodic Table.

15.4 OCCURRENCE AND APPLICATIONS OF LANTHANIDES

Monazite sand found on the Travancore coast in South India is an easy source fo a number of lanthanides It is mainly cerium phosphate, $CePO_4$. It has about 50 t 75% of oxides of cerium group. It has also 5 to 9% of thoria (ThO_2) and traces uranium After extraction, the constituents are separated by ion exchange techniques

The pure metals have no specific use and hence lanthanide metals are extracted as mixtures or alloys. These are called mischmetals. Cerium may constitute 30 to 50% of these alloys. They are used for scavenging oxygen and sulphur from other metals. Addition of about 3% mischmetal to magnesium increases its strength and makes it useful for jet engine parts. Mischmetal imparts high temperature strength to aluminium, hardness to copper, lathe workability to stainless steel and oxidation resistance to nickel.

Alloyed with 30% iron mischmetal becomes sufficiently pyrophoric for use in lighter 'stones' or 'flints'.

Lanthanide oxides are used for polishing glass. Neodymium and praseodymium oxides are used for making coloured glasses for goggles. These goggles are particularly useful for glass blowers as they absorb the bright yellow sodium light.

Lanthanide compounds are found to be good catalysts for hydrogenation, dehydrogenation, oxidation, and petroleum cracking processes. They are also used in magnetic and electronic devices for their para-and ferro-magnetic properties. They are filled into arc carbon electrodes for greater brilliance. Gas lamp mantles also make use of ceria and thoria.

15.5 THE ACTINIDES

There are 14 elements following actinium, Ac, (atomic number : 89). Electronic configurations of these elements show even more frequent irregularities than the lanthanides (Table 15.2).

TABLE 15.2

Electronic Configurations of Actinides

Element	*Symbol*	*Atomic number*	*Electronic configuration*
Actinium	Ac	89	$6d^17s^2$
Thorium	Th	90	$5f^06d^27s^2$
Protoactinium	Pa	91	$5f^26d^17s^2$
Uranium	U	92	$5f^36d^17s^2$
Neptunium	Np	93	$5f^46d^17s^2$
Plutonium	Pu	94	$5f^66d^07s^2$
Americium	Am	95	$5f^76d^07s^2$
Curium	Cm	96	$5f^76d^07s^2$
Berkalium	Bk	97	$5f^96d^07s^2$
Californium	Cf	98	$5f^{10}6d^07s^2$
Einsteinium	Es	99	$5f^{11}6d^07s^2$
Fermium	Fm	100	$5f^{12}6d^07s^2$
Mendelevium	Md	101	$5f^{13}6d^07s^2$
Nobelium	No	102	$5f^{14}6d^07s^2$
Lawrencium	Lr	103	$5f^{14}6d^17s^2$

Most of these elements have been made by bombardment of available nuclei by accelerated sub-nuclear particles. They are all radioactive metals. Close resemblances between actinides and corresponding lanthanides have been very helpful in characterizing and separation of actinides which could be synthesized in very small amounts

From point of abundance in igneous rocks, thorium is the most abundant, being about 1.15×10^{-3} %; uranium comes next, 4×10^{-4} %. The non-existence of most of actinides in nature is attributed to their relatively short half-lives.

The main source of thorium is the monazite sands of Travancore Uranium is recovered from pitch blende which occurs along with other minerals. Plutonium is one of the elements made in atomic reactors on a large scale from Uranium-238

$$ {}^{238}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \longrightarrow {}^{239}_{92}\mathrm{U} \xrightarrow{-\beta} {}^{239}_{93}\mathrm{Np} \xrightarrow{-\beta} {}^{239}_{94}\mathrm{Pu} $$

stable unstable unstable stable

$t_{\frac{1}{2}} = 4.5\times 10^{9}$ yrs $t_{\frac{1}{2}} = 25$min $t_{\frac{1}{2}} = 2.33$ days $t_{\frac{1}{2}} = 2.4\times 10^{4}$ years

Plutonium being chemically different from uranium, can be easily separated from it. Uranium-238 is not a fissionable isotope. On the other hand, like U-235, plutonium-239 is fissionable under bombardment by slow neutrons and can be stored and used as needed. Thus the more abundant and therefore cheaper uranium-238 isotope has been converted to the much more useful plutonium-239. Plutonium-239 is a material of trade between nations interested in generation of atomic energy.

Thorium-232 can also be converted to fissionable uranium-233 by a similar series of steps in a reactor;

$$ {}^{232}_{90}\mathrm{Th} + {}^{1}_{0}\mathrm{n} \longrightarrow {}^{233}_{90}\mathrm{Th} $$

$$ {}^{233}_{90}\mathrm{Th} \xrightarrow{t_{\frac{1}{2}} = 22\mathrm{min}} {}^{233}_{91}\mathrm{Pa} + {}^{0}_{-1}\mathrm{e} $$

$$ {}^{233}_{91}\mathrm{Pa} \xrightarrow{t_{\frac{1}{2}} = 27\ \mathrm{days}} {}^{233}_{92}\mathrm{U} + {}^{0}_{-1}\mathrm{e} $$

$$ {}^{233}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \longrightarrow \text{Fission products} + \text{energy} $$

U-233 has a half life of 1.6×10^{5} years.

Uranium salts impart green colour to glass. Thorium as oxide is used in making gas manules. The mantle woven from silk fibres is dipped into a mixed solution of thorium and cerium nitrates in the ratio of 99 and 1% respectively. It is dried and sold in this form. When fixed in the lamp and ignited for the first time, the silk fibres burn away leaving behind a net work of ThO_2 (thoria) and CeO_2 (ceria) in the form of a rather brittle bag. Both these oxides can withstand high temperatures.

Plutonium is fissionable material (fuel) used in atomic energy plants. After use it is again enriched by chemical separation from products and reused. As it can also be used for making atomic bombs, atomic energy plants are sought to be internationally controlled.

Exercise 15.1

Plutonium-239 undergoes a fission reaction by absorbing a thermal neutron and 3 new neutrons are given up in this reaction. Suggest a way in which this could happen if Kr-94 isotope is one product.

Solution

The fission of U-235 may be represented in about 30 different ways. Two of these are presented as :

$${}^{235}_{92}\text{U} + {}^{1}_{0}\text{n} \longrightarrow {}^{103}_{42}\text{Mo} + {}^{131}_{50}\text{Sn} + 2\,{}^{1}_{0}\text{n}$$

$${}^{235}_{92}\text{U} + {}^{1}_{0}\text{n} \longrightarrow {}^{139}_{56}\text{Ba} + {}^{94}_{36}\text{Kr} + 3\,{}^{1}_{0}\text{n}$$

The essential requirements in the fission reaction are:

(i) Total of mass numbers must be unaltered.

(ii) Total of proton numbers must be unaltered.

(iii) The product atoms should be of about half mass number.

For Pu-239 after gaining one neutron and losing 3 neutrons, mass to be distributed will be 237. The protons to be distributed will be 94. Atomic number of Kr-94 is 36. Atomic number of the other element will be 58. Isotopic mass will be 143.

$${}^{239}_{94}\text{Pu} + {}^{1}_{0}\text{n} \longrightarrow {}^{94}_{36}\text{Kr} + {}^{143}_{58}\text{Ce} + 3\,{}^{1}_{0}\text{n}$$

15.6 TRANSACTINIDE ELEMENTS

The actinide series was completed with the synthesis of lawrencium, Lr (atomic number : 103). The synthesis of elements with atomic numbers 104 and 105 has started the filling up of 6*d*-transition series. The names of some of these elements have not been finally accepted. Russians have proposed the names *joliocium* for element 102, *kurchatovium* for element 104 while the Americans would like to call them *nobelium* and *rutherfordium*, respectively. American proposal for name of element 105 is *hahnium*. Remembering the days of Mendeleev, the newly made elements are also being named as 'eka'—elements. The 6*d* series should complete with element 112 (eka-mercury) and then 7*p*-orbitals should be filled for elements from 113 to 118. This would be followed by the $8s^1$ and $8s^2$ configurations. Most of these new elements are expected to be very short lived. However, the stability observed with elements having atomic numbers corresponding to *magic numbers** hold out a hope for relatively stable elements with atomic numbers 114 (eka-lead) and 164 (dvi-lead). This extension of the periodic table will need the 9*g*-orbitals. The corresponding elements would need another special location in the table as a *g*-block.

EXERCISES

15.1 What is the difference in the electronic structures of transition and inner-transition elements?

15.2 Which of the elements beyond lawrencium, Lr, (atomic number: 103) will belong to the *d*-and *p*-blocks?

15.3 What will be the atomic numbers of two more elements of zero group after radon (atomic number: 86)?

15.4 Explain the terms. lanthanides, actinides, rare earths, nuclear fuels, eka-mercury, magic numbers.

15.5 What is meant by lanthanide contraction and why does it occur?

15.6 Why no industry is run to separate the elements of 4*f*-series and 5*f*-series from the respective mixtures?

15.7 List the uses of lanthanides.

15 8 How is plutonium obtained and to what use is it put?

15.9 Uranium salts are ordinary chemicals but production of atomic energy from uranium is an expensive method. Explain.

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*It has been found that atomic nuclides with certain numbers of neutrons or protons are much more stable than others. Such numbers have been nick named as *magic numbers*. They are 2, 8, 20, 50, 82, 126, 164, etc.

UNIT 16

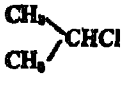
Alkyl and Aryl Halides

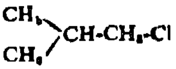
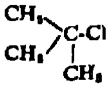
Alkyl halides are compounds of the general formula R-X where R stands for an alkyl group and X stands for any of the halogen atoms. They can be regarded as substituted alkanes in which one of the hydrogen atoms attached to the carbon chain is replaced by one of the halogen atoms. There are marked differences in the methods of preparation and properties of alkyl fluorides and other halogen substituted alkanes, therefore the alkyl fluorides and other fluorocarbons are dealt with separately. Here we shall be dealing with alkyl chlorides, bromides and iodides which are closely similar in their method of preparation and reactions.

Aryl halides are the compounds in which a halogen atom like Cl, Br or I is linked to an aromatic ring replacing a hydrogen atom. Thus, C_6H_5Cl and $ClC_6H_4CH_3$, in which the chlorine atom is attached to one of the carbons of the aromatic benzene ring, are examples of aryl chlorides.

16.1 NOMENCLATURE

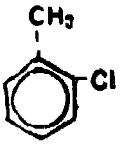
The trivial and IUPAC names of the first few alkyl halides are as follows :

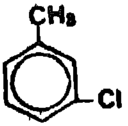
Formula	*Trivial name*	*IUPAC name*
CH_3Cl	methyl chloride	chloromethane
CH_3CH_2Cl	*ethyl chloride*	chloroethane
$CH_3CH_2CH_2Cl$	*n*-propyl chloride	1-chloropropane
 $(CH_3)_2CHCl$	*iso*-propyl chloride	2-chloropropane
$CH_3CH_2CH_2CH_2Cl$	*n*-butyl chloride	1-chlorobutane
$CH_3-\underset{\mid \atop Cl}{CH}-CH_2CH_3$	*sec*-butyl chloride	2-chlorobutane

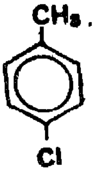
Formula	*Trivial name*	*IUPAC name*
 $(CH_3)_2CH\text{-}CH_2\text{-}Cl$	*iso*-butyl chloride	1-chloro-2-methyl propane
 $(CH_3)_3C\text{-}Cl$	*tert*-butyl chloride	2-chloro-2-methyl propane

Thus in the trivial system of nomenclature, an alkyl halide is named by adding the trivial name of alkyl group to the halide name. In the IUPAC system the halogen is regarded as a substituent and the halohydrocarbons are given one word names. The substitution by bromine or iodine in place of chlorine in the tabulated compounds will lead to the formation of the corresponding bromo- or iodo-hydrocarbons.

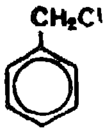
Chlorobenzene is the first member of the group of aryl halides. The next higher homologue is obtained by displacing one of the hydrogens on the ring in toluene by a halogen atom. Such a replacement can take place at *ortho*, *meta* or *para* position with respect to the methyl group. Consequently the following three isomers are possible for chlorotoluene.


o-chlorotoluene
(2-chlorotoluene)


m-chlorotoluene
(3-chlorotoluene)


p-chlorotoluene
(4-chlorotoluene)

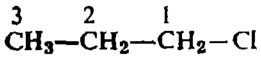
The displacement of one of the hydrogens of methyl group will yield the fourth isomer, benzyl chloride,


benzyl chloride

which, is considered an alkyl halide and not an aryl halide because the halogen is not directly attached to the benzene ring.

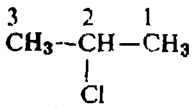
16.2 MORE ABOUT ISOMERISM

We have already discussed the phenomenon of structural isomerism in alkanes in Section 16.2 of Part I Such isomers are compounds which have the same molecular formula but different structural formulae, resulting from the difference in the sequence in which the atoms of the molecules are bonded together With the introduction of a halogen atom in the molecule a new possibility of isomerism arises according to the position of halogen atom on the carbon chain This type of isomerism is referred to as *position isomerism*. 1-chloropropane and 2-chloropropane are two position isomers having identical carbon chains but different locations of the halogen atom.



$$\overset{3}{C}H_3-\overset{2}{C}H_2-\overset{1}{C}H_2-Cl$$

1—chloropropane

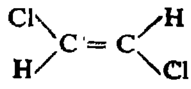


$$\overset{3}{C}H_3-\underset{Cl}{\overset{2}{C}H}-\overset{1}{C}H_3$$

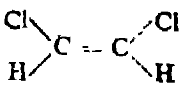
2—chloropropane

Isomerism may, however, also result from different orientation of atoms or groups in space in a molecule. This type of isomerism is called spatial isomerism or *stereoisomerism*.* The isomers resulting from different spatial arrangements of atoms or groups of atoms in space are called *stereoisomers*

We may recall that in geometrical isomerism (*cis-trans isomerism*) too the isomers have the same structural formulae, but as a result of restricted rotation about the double bond, two different spatial arrangements of the atoms or groups of atoms in the molecules are possible Geometrical isomerism is thus a kind of stereoisomerism, ptical isomerism is another type of stereoisomerism. This interesting and subtle type f isomerism is shown by substances whose molecules are *dissymmetric*. A dissymmetric molecule is one which cannot be super-imposed on its mirror image like letter p and unlike A (Fig. 16.1) An example of an object not being superimposable on its mirror image is the human hand. Right hand is a mirror image of the left



trans-dichloroethylene



cis-dichloroethylene

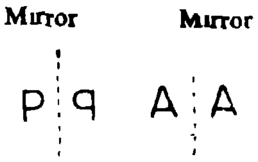


Fig. 16.1 Non-superimposable and superimposable mirror images

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*Stereo—meaning space.

The two hands can be placed face to face but not one over the other in a coinciding manner. Compare this situation with a button. Because of the symmetrical shape a button will coincide with another button which may be its mirror image.

All objects, like the human hand, which do not superimpose on their mirror images are said to be dissymmetric objects.

Dissymmetry in carbon compounds is a consequence of the tetrahedral geometry of the sp^3 hybridized carbon atom. The idea that carbon atom forms four bonds directed towards four corners of a tetrahedron was first put forward by LeBel and van't Hoff in 1873. A tetrahedral model of fluorochlorobromomethane and its mirror image are shown in Fig. 16.2.

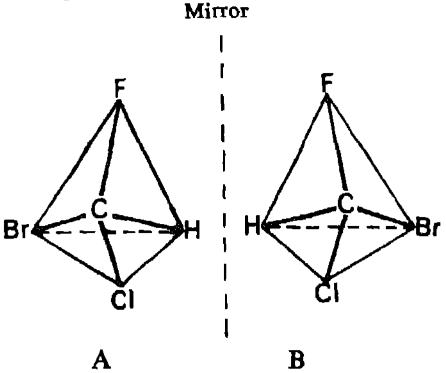

Fig. 16.2 Fluorochlorobromomethane and its mirror image

In this case the four atoms attached to the carbon atom are all different. The A and B arrangements given here are related to each other as an object and its mirror image We find that no rotational motion around any axis, or any other manipulation except cleavage of bonds can make one model superimposable on the other.* Each one of

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*In case any two groups attached to a carbon atom are similar as in dichlorofluoromethane, the molecule no longer remains dissymmetric and a simple rotational motion around an axis would make it superimposable on its mirror image. Students can satisfy themselves by handling actual models. In Fig. 16.3, model A will become superimposable on model B, if it is rotated through an angle of 120° such that the atom H will come into the position of $\overset{1}{\text{Cl}}$, the atom $\overset{1}{\text{Cl}}$ will take the position of $\overset{2}{\text{Cl}}$ and the atom $\overset{2}{\text{Cl}}$ will take the position of atom H. Position of atom F will remain undisturbed.

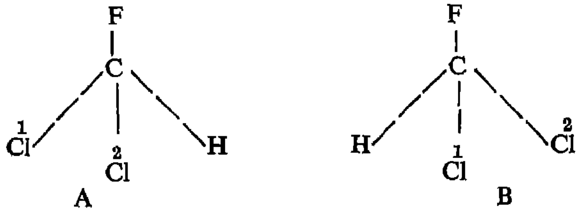
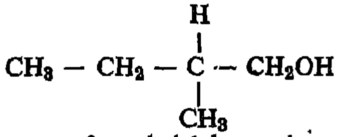


Fig. 16.3 A and B depicting two positions of dichloroflurومethane

these arrangements of atoms represents a stereoisomer, not superimposable on its mirror image; fluorochlorobromomethane is thus a dissymmetric molecule Stereoisomers related to each other as two non-superimposable spatial arrangements are described as *enantiomers* Enantiomers have mostly identical physical and chemical properties but will differ in shapes of crystals, optical rotations and biological activities. Table 16.1 shows some of the physical properties of 2-methyl-1-butanol



$$CH_3 - CH_2 - \overset{H}{\underset{CH_3}{C}} - CH_2OH$$

2 methyl-1-butanol

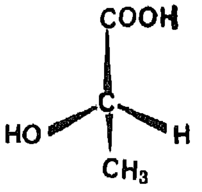
enantiomers in which carbon number 2 is attached to four different groups i e., H, CH_2OH, CH_3 and C_2H_5 This carbon provides an asymmetry centre in the molecule. Any carbon atom in a molecule which is tetrahedrally linked to four different atoms or groups is called an *asymmetric carbon* atom.

TABLE 16.1

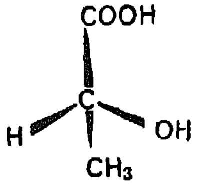
Physical Properties of Enantiomers

	(+) 2 methyl-1-butanol	(—) 2 methyl-1-butanol
Specific optical rotation	+5.756°	—5.756°
b. p.	401.9K	401.9K
Density	0.8193	0.8193
Refractive index	1.4173	1.4173

A convenient method of distinguishing between the two enantiomers of a substance is their behaviour towards plane polarised light. When enantiomers (as such if liquids, or as solutions if solids) are placed in the path of a beam of polarised light, they will rotate the plane of the polarised light in opposite directions to an equal extent. The enantiomer which rotates this plane to the right is called *dextro(+)rotatory* and the other which rotates it to the left is called *laevo (—) rotatory*. Dextro and laevo forms of a substance are denoted by the letters *d*- and *l*- respectively. The two enantiomers of lactic acid are shown below :



(+) Lactic acid



(—) Lactic acid

We are familiar that ordinary light is composed of light waves of different wavelengths Monochromatic light (i e light of only one wavelength) can be obtained by passing ordinary white light through a prism or grating. It can also be obtained by using a lamp which gives light of only one wavelength e.g., a sodium lamp emits yellow light of about 589.3nm wavelength. Whether it is ordinary light or monochromatic radiation it is composed of waves which are vibrating in a number of different planes passing through the line of propagation. If such a beam of light is passed through a device such as Nicol Prisms *(named after discoverer) it can be converted to plane polarised light in which vibrations take place only in one plane.

If a beam of plane polarised light is passed through a dissymmetric material, the plane of polarisation is changed. The asymmetric material is thus called optically active The isomers which differ in their behaviour towards plane polarised light, are called optical isomers The phenomenon of existence of optical isomers is called *optical isomerism.*

This rotation of plane polarised light or optical activity can be detected and measured by an instrument known as *polarimeter.*

16.2-1 RACEMIC MIXTURES

If a substance is found to be optically inactive in a polarimeter, it does not necessarily mean that it must have symmetric molecules. Optical inactivity can also be observed if equal amounts of dextro and laevo enantiomers are mixed together, one tends to rotate the plane of the polarised light to the right, the other, to an equal extent to the left and the net effect is that no optical rotation is observed. Such a mixture of *d*-and *l*-enantiomers is called a racemic mixture or modification and is denoted as *dl* or (±) form A racemic mixture may be formed by mechanically mixing the two enantiomers in equal quantities. In most organic synthesis, racemic products are formed instead of pure optically active enantiomers. This is due to the equal probabilities of formation of the two enantiomers. However, in the biological systems where most of the synthesis are done with the help of enzymes, usually only one enantiomer of a substance is produced This type of synthesis in which only one enantiomer of an asymmetric substance is produced is known as *asymmetric synthesis.* All the amino acids present in higher animals are laevo amino acids. Glucose from grapes and cane sugar from sugarcane are both found to be dextrorotatory. Racemic modifications can be separated into *d*-and *l*-enantiomers under suitable conditions. This process of separation is called *resolution*

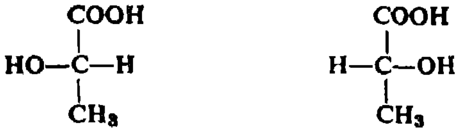
Nicol prisms are made from a particular crystalline form of $CaCO_3$ known as calcite. A rhomb of calcite is cut from corner and then cemented back by canada balsam.

16.2-2 CONFIGURATION

We have seen above that enantiomer pairs represent two different spatial arrangements of substituents at an asymmetric carbon atom. Each one of these arrangements is called a *configuration.*

You will recall that one needs structural formulae to describe organic molecules, molecular formulae alone are not sufficient Among stereoisomers even structural formulae fail to completely define the isomers, since the arrangements of atoms or groups in space are also important in case of stereo isomers. Fischer proposed a specific orientation in which an enantiomer molecule be held for writing its projected formula.

In Fischer projection, the molecule is so held that its asymmetric carbon is in th plane of the paper, the groups at the top and bottom are inclined equally *below* this plane, and the group on the left and right are similarly inclined equally *above* the plane. The groups attached to the asymmetric carbon in the molecule are then projected on to the plane in the shape of a cross. The Fischer projection formula for lactic acid (shown on page 217) is given below.



$$\begin{array}{c} COOH \\ | \\ HO-C-H \\ | \\ CH_3 \end{array} \qquad \begin{array}{c} COOH \\ | \\ H-C-OH \\ | \\ CH_3 \end{array}$$

d- lactic acid or L (+) lactic acid

l- lactic acid or D (—) lactic acid

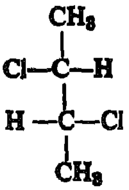
Fischer projection formula for lactic acid

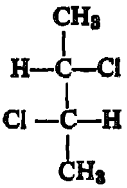
In these Fisher projection formulae, the enantiomers having the OH group on the right hand side is designated by the letter D and other having the OH group on the left is designated by the letter L The symbols D and L are indicative of spatial distributions around the first asymmetric carbon atom from the bottom but not the optical rotating power of the molecule. The optical rotating power of substances can be indicated by adding the (+) sign for dextro-rotation and (—) sign for laevo-rotation. Thus d-lactic acid i.e. dextrorotatory acid can also be represented as the L (+) lactic acid. From similar consideration (*l*-), lactic acid in which H and OH on the asymmetric carbon are in reverse positions with respect to dextro-lactic, acid will be represented by D (—) lactic acid.

D (+) and L(—), and D(—) and L(+) enantiomers may also be possible in compounds which contain more than one asymmetric carbon atoms.

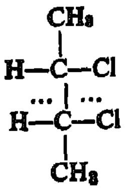
16.2-3 MANY ASYMMETRIC CENTRES PER MOLECULE

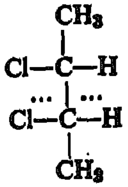
Compounds that contain two or more asymmetric centres can exist in more than two stereoisomeric forms. In 2, 3-dichlorobutane two asymmetric carbon atoms (2 and 3) are present. Using the models we can write the following structures:


(1)


(2)

Non-Superimposable (enantiomers)

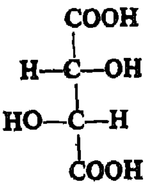

(3)

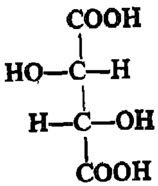

(4)

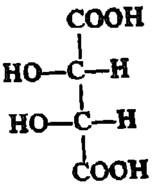
(Superimposable *meso*-form)

Structures (1) and (2) are non-superimposable mirror images and these are therefore enantiomers. However, the structures (3) and (4) are superimposable mirror images and therefore are not asymmetric, even though the asymmetric carbon atoms are present in them. They have a plane of symmetry as indicated by dotted lines. Such stereo isomers are called ,meso-forms. Because of the symmetry in meso forms, the optical rotation due to one asymmetric carbon atom exactly counteracts the optical rotation due to other asymmetric carbon atom. The *meso* enantiomers are optically inactive, and like the racemic modifications, they can not be resolved into optically active enantiomers.

Tartaric acid is another common example of a substance existing in dextro, laevo and meso forms.


dextro


laevo


meso

tartaric acids

16.3 PREPARATIONS OF ALKYL HALIDES

For laboratory preparation of alkyl halides the starting materials are generally alcohols, or hydrocarbons.

1. Alkyl halides from alcohols

$$ROH \rightarrow RX$$

This is a substitution reaction. Various reagents can be used to replace the hydroxyl group in alcohols by a halogen atom. Some of these are :

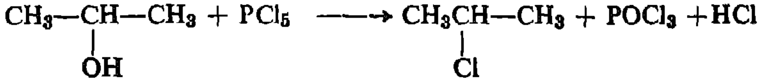
(a) *Reactions with hydrogen halides and concentrated hydrohalogen acids* : These react with alcohols under dehydrating conditions which help in preventing the reverse reaction with water. The reactivity of acids is in the order HI> HBr> HCl and of alcohols is in the order tertiary>secondary>primary.

$$CH_3CH_2OH + HCl \xrightarrow{ZnCl_2} CH_3CH_2Cl + H_2O$$

$$CH_3CH_2OH + NaBr + H_2SO_4 \longrightarrow CH_3CH_2Br + H_2O + NaHSO_4$$

(b) *Reactions with phosphorus halides and thionyl chloride* : A mixture of red phosphorus with Br_2 or I_2 is taken for providing PBr_3 or PI_3.

$$CH_3CH_2CH_2OH + SOCl_2 \longrightarrow CH_3CH_2CH_2Cl + SO_2 + HCl$$



$$CH_3{-}\underset{\displaystyle OH}{\underset{|}{CH}}{-}CH_3 + PCl_5 \longrightarrow CH_3\underset{\displaystyle Cl}{\underset{|}{CH}}{-}CH_3 + POCl_3 + HCl$$

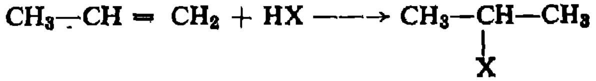
$$CH_3CH_2CH_2OH + P/I_2 \longrightarrow CH_3CH_2CH_2I + H_3PO_3$$

Thionyl chloride is preferred in the preparation of chloro compounds since both the by-products in such reactions are gases, and make the purification of the final product easy.

2. Alkyl halides from hydrocarbons

(a) A treatment of alkanes with halogens gives a mixture of mono and poly-substitution products. It is quite difficult to separate such mixtures.

(b) Alkenes can add hydrogen halides to form alkyl halides.



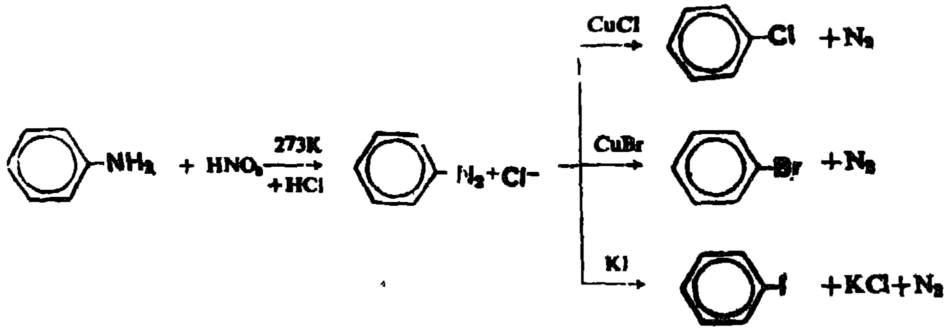
$$CH_3{-}CH = CH_2 + HX \longrightarrow CH_3{-}\underset{\displaystyle X}{\underset{|}{CH}}{-}CH_3$$

The above addition reactions proceed in accordance with Markownikoff's rule (Part I). According to this rule the hydrogen part of hydrogen halide attaches to the double bond carbon which has already more of hydrogen atoms attached to it.

In the presence of organic peroxides, the addition of hydrogen bromide (not of HCl or HI) to alkenes proceeds by a different mechanism and gives a different product. In the presence of benzoyl peroxide, HBr gives 1-bromo propane, as the major product. This addition is called *anti-Markownikoff's addition* (Kharasch effect), since the orientation of bromine in the resulting compound is different from that in ionic addition according to Markownikoff's rule.

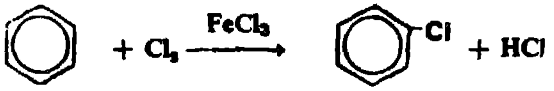
16.4 PREPARATION OF ARYL HALIDES

Aromatic halides cannot be prepared from phenols, since replacement of phenolic hydroxyl group by a halogen atom is not easy. They can be conveniently prepared from aromatic amines. The replacement of amino group in aryl amines by a halogen atom cannot be done directly. The amino compounds are first reacted with nitrous acid ($NaNO_2$ + HCl or H_2SO_4) at low temperatures. The resulting diazonium salt is treated with CuCl, CuBr, or KI to give the corresponding aryl halide. This reaction will be discussed in detail in Unit 18.



Although more expensive, this method has the advantage over direct halogenation, as the product is not contaminated with disubstituted *o*-and *p*-isomers, or with di, or polysubstituted compounds.

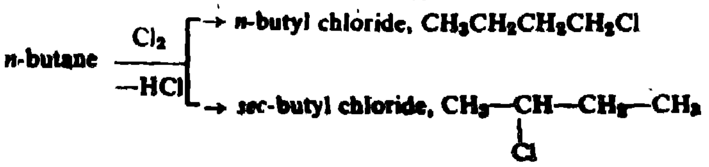
Aryl halides can also be prepared by direct halogenation using a Lewis acid as catalyst (Part I). Direct halogenation of benzene ring is more useful than direct halogenation of alkanes. However, fluorides and iodides cannot be obtained by this method. The mechanism of this reaction has been discussed in Part I.



16.5 INDUSTRIAL PREPARATIONS

(a) The alkyl chlorides on industrial scale are prepared by direct chlorination of hydrocarbons at high temperatures. The free radical mechanism by which these reactions proceed has already been discussed (Part I).

$$CH_4 \xrightarrow[-HCl]{Cl_2} CH_3Cl \xrightarrow[-HCl]{Cl_2} CH_2Cl_2 \xrightarrow[-HCl]{Cl_2} CHCl_3 \xrightarrow[-HCl]{Cl_2} CCl_4$$



n-butane $\xrightarrow[-HCl]{Cl_2}$ → *n*-butyl chloride, $CH_3CH_2CH_2CH_2Cl$

→ *sec*-butyl chloride, $CH_3-CH(Cl)-CH_2-CH_3$

In this substitution reaction, mixtures of isomers and poly substitution products are generally formed. Since most of these chlorine derivatives are used as industrial solvents, the mixtures obtained by direct chlorination can be used as such without separation into individual components. Pure components can sometimes be separated by fractional distillation.

(b) Some of the unsaturated alkyl halides which find applications in the preparation of polymers are obtained by addition reactions instead of direct substitution. Thus vinyl chloride can be obtained by addition of HCl to acetylene in presence of $HgCl_2$ (Part I).

$$CH \equiv CH + HCl \xrightarrow{HgCl_2} \underset{\text{vinyl chloride}}{CH_2 = CHCl}$$

The methods for the preparation of fluoro derivatives of hydrocarbons are very different from those for the corresponding chloro or bromo compounds. Usually alkanes are reacted with inorganic fluorides resulting in substitution of one or more hydrogen atoms. You will learn about details of such preparations in your later classes.

16.6 PHYSICAL PROPERTIES

The molecular masses of alkyl halides are higher than that of the corresponding alkanes. Consequently the melting points and boiling points of these compounds are several degrees higher than the parent alkanes. Following order is observed in the boiling points of alkyl halides according to the halogen contained by them.

$$RF < RCl < RBr < RI$$

The physical constants of some alkyl halides are given in Table 16.2

TABLE 16.2

Physical Constants of Some Alkyl Halides

Name of alkyl radical	*CHLORIDE*		*BROMIDE*		*IODIDE*	
	b. p. (K)	*Density at 293K (g/cm^3)*	*b. p. (K)*	*Density at 293K (g/cm^3)*	*b. p. (K)*	*Density at 293K (g/cm^3)*
methyl	249.0	gas	278	gas	315	2.279
ethyl	285.0	gas	311	1.440	345	1.933
n-propyl	320.0	0.890	344	1.335	375	1.747
iso-propyl	313.5	0.859	333	1.310	362.5	1.705
n-butyl	351.5	0.884	375	1.276	403	1.617
iso-butyl	342.0	0.875	364	1.261	394	1.605
sec-butyl	341.0	0.871	364	1.258	392	1.595
tert-butyl	324.0	0.840	346	1.222	373 (d)	—

Although polar in nature, alkyl halides are insoluble in water due to their inability to form hydrogen bonds with water molecules or to break the hydrogen bonds already existing in water. They are soluble in organic solvents. Alkyl chlorides are generally lighter than water whereas alkyl bromides and iodies are generally heavier. Methyl iodide is the densest alkyl halide as in this compound iodine has its greatest density contribution relative to the contribution of the hydrocarbon part.

The physical properties of aryl halides are similar to those of the corresponding alkyl halides. They are insoluble in water, acids or bases and are soluble in organic solvents. The boiling points of isomeric dihalobenzenes are very nearly the same (Table 16.3). But the melting points of these compounds show a considerable spread. In each case the *para* isomer melts at 70-100 degrees higher than the *ortho* and *meta* isomers. The *para* isomer is more symmetrical and therefore can fit better in the crystal lattice of the solid forms. Due to the higher intracrystalline forces the *para* isomers are also less soluble in a given solvent than the *ortho* isomers.

TABLE 16.3

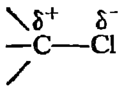
Physical Constants of Some Aryl Halides

Name of Aryl Halide	*ORTHO*		*META*		*PARA*	
	m. p. (K)	*b. p.* (K)	*m. p.* (K)	*b.p.* (K)	*m. p.* (K)	*b. p.* (K)
Chlorotoluene	226	432	225	435	281	435
Bromotoluene	246	455	233	454	301	458
Iodotoluene	—	479	—	484	308	484
Dichlorobenzene	256	453	249	446	325	448
Dibromobenzene	279	494	266	490	360	492
Diiodobenzene	300	560	308	558	402	558

16.7 CHEMICAL PROPERTIES

A large number of organic compounds with different functional groups can be prepared from alkyl halides. Halobenzenes and vinyl halides, on the other hand, are much less reactive and undergo reactions only under drastic reaction conditions as in alkyl halides. The carbon carrying the halogen atom is sp^3 hybridized while in aryl and vinyl halides it is sp^2 hybridized

Organic halogen compounds are polar in nature. The more electronegative halogen atom withdraws the shared pair of electrons towards its side.



The electron density around halogen is increased and the bonded carbon which becomes deficient in electron density, acquires a partial positive charge. The dipole moments of alkyl halides range from 2.05 to 2.15D. The dipole moment of chlorobenzene is 1.73d and that of vinyl chloride is 1.44D.

16.7-1 HALOGEN REPLACEMENT REACTIONS

The typical reactions of alkyl halides are replacement reactions Electron rich reagents (nucleophiles) attack the alkyl halides. The weakly basic halide ion is displaced. Such reactions in which a strong nucleophile displaces a weaker nucleophile from the substrate, are called *nucleophilic displacement reactions.* A wide variety of important products can be prepared by using different types of nucleophiles and alkyl halides. In Table 16.4 some of these reactions are summarised

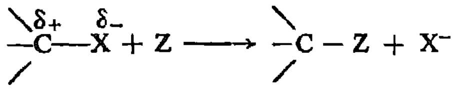


TABLE 16.4

Typical Reactions of Alkyl Halides

$$RX + E{-}Nu \longrightarrow R{-}Nu + EX$$

Alkyl halides	*Reagent E-Nu*	*Product R-Nu*	*Class*	*Other Product (EX)*
RX	HOH	ROH	alcohol	HX
	NaOH	ROH	alcohol	NaX
	NaOR	ROR	ether	NaX
	HOR	ROR	ether	HX
	KI	RI	alkyl iodide	KX
	$H{-}NH_2$	$R{-}NH_2$	amine	HX
	Na-SH	RSH	mercaptans	NaX
	H-SR	R-S-R	thioethers	HX
	K-CN	R-CN	alkyl cyanide	KX
	Ag-CN	$R{-}N{\equiv}C$	alkyl isocyanide	AgX
	$K{-}NO_2$	$R{-}NO_2$	nitroalkane	KX
	$Ag{-}NO_2$	RONO	alkylnitrite	AgX

Alkyl halides thus serve as the starting materials for the preparation of many different classes of organic compounds Nucleophilic substitution of alkyl halides is one of the most useful organic reactions.

Nucleophilic aromatic substitutions are much less important in synthesis due to the low reactivity of aryl halides. Chlorobenzene is converted to phenol by aqueous NaOH and reacting under pressure at temperatures over 575K The presence of nitro group at *o*-or *p*-position to halogen greatly enhances the reactivity.

16.7-2 DEHYDROHALOGENATION REACTIONS

We have mentioned about these reactions in the preparation of alkenes from alkyl halides using ethanolic KOH (Part I).

$$\overset{\beta}{C}H_3\overset{\alpha}{C}H_2X \xrightarrow{OH^-} CH_2 = CH_2 + H_2O + X^-$$

The yield of alkene is fair with primary halides and very good for secondary and tertiary halides.

Such dehydrohalogenation reactions are classified as β-elimination reactions as the hydrogen atom is eliminated from the β-carbon in the molecule.

16.7-3 REACTION WITH MAGNESIUM

When a solution of an alkyl halide in diethyl ether is allowed to stand over magnesium turnings, the metal gradually dissolves and an organometallic substance, R-Mg-X is formed This reagent was developed by Victor Grignard*. Such compounds are named after him as Grignard reagents.

$$CH_3Br + Mg \xrightarrow{\text{ether}} \underset{\text{methyl magnesium bromide}}{CH_3MgBr}$$

$$CH_3CH_2I + Mg \xrightarrow{\text{ether}} \underset{\text{ethyl magnesium iodide}}{CH_3CH_2MgI}$$

Aryl and vinyl halides also yield Grignard reagents, but less readily than in case of alkyl halides. A high boiling solvent such as tetrahydrofuran is used in these preparations, in place of ether.

$$C_6H_5X + Mg \longrightarrow C_6H_5MgX$$

In Grignard compounds the C—Mg bond is a covalent one, but is highly polar in character.

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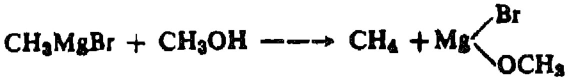
* Grignard received Nobel Prize in 1912 for developing this reagent.

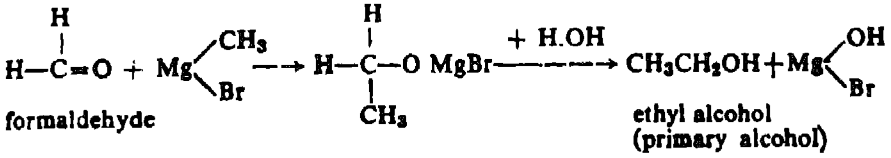
Grignard reagents are very reactive. They react with several inorganic compounds including water, CO_2, and oxygen, and a variety of organic compounds. Two types of reactions are common :

(a) Reactions with compounds having active hydrogen atoms such as alcohols, water, acids, etc. In these reactions the alkyl or aryl group of Grignard reagent always combines with the active hydrogen atom to form a hydrocarbon, RH.

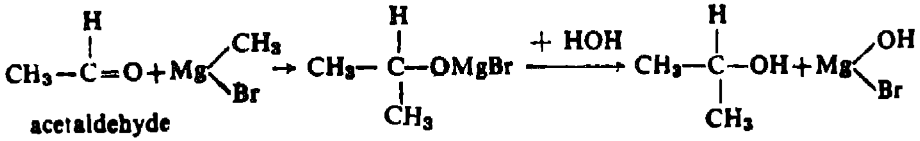


$$CH_3MgBr + CH_3OH \longrightarrow CH_4 + Mg\Big\langle^{Br}_{OCH_3}$$

(b) Addition to a carbonyl group as in aldehydes and ketones followed by reaction with water :

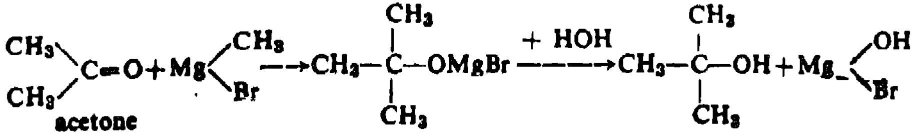


$$\underset{\text{formaldehyde}}{H-\overset{H}{\overset{|}{C}}=O} + Mg\Big\langle^{CH_3}_{Br} \longrightarrow H-\overset{H}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-O\ MgBr \xrightarrow{+\ H.OH} \underset{\substack{\text{ethyl alcohol}\\ \text{(primary alcohol)}}}{CH_3CH_2OH} + Mg\Big\langle^{OH}_{Br}$$



$$\underset{\text{acetaldehyde}}{CH_3-\overset{H}{\overset{|}{C}}=O} + Mg\Big\langle^{CH_3}_{Br} \rightarrow CH_3-\overset{H}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-OMgBr \xrightarrow{+\ HOH} CH_3-\overset{H}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-OH + Mg\Big\langle^{OH}_{Br}$$

As we will see in the next Unit, this reaction is very useful in the synthesis of alcohols of various types



$$\underset{\text{acetone}}{\begin{matrix}CH_3\\ CH_3\end{matrix}\Big\rangle C=O} + Mg\Big\langle^{CH_3}_{Br} \longrightarrow CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-OMgBr \xrightarrow{+\ HOH} CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-OH + Mg\Big\langle^{OH}_{Br}$$

16.7-4 REACTION WITH SODIUM

When an alkyl halide reacts with sodium metal in dry ether, a hydrocarbon is formed.

$$2RX + 2Na \longrightarrow 2NaX + R-R$$

This reaction is called *Wurtz reaction.*

16.7-5 REDUCTION

The alkyl halides can be converted to alkanes by using suitable reducing agents (HI + P, H_2 + catalyst, Zn + HCl, etc.).

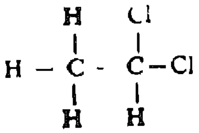
$$R-X + H_2 \longrightarrow R-H + HX$$

16.8 POLYHALOGEN DERIVATIVES

Alkyl halides are basically monohalogen substitution derivatives of hydrocarbons; Some other halogen derivatives having more than one halogen atoms per molecule are also useful compounds. These are collectively called polyhalogen derivatives. Described below are a few of the commercially useful compounds of this series.

16.8-1 DICHLOROETHANES

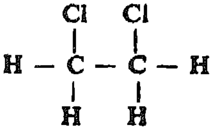
Two dichloroethanes are possible. 1, 1-dichloroethane and 1, 2-dichloroethane. The former has both the chlorine atoms attached to the same carbon, $CH_3—CHCl_2$, and the latter has them on the two different carbons, $CH_2Cl—CH_2Cl$.



$$\begin{array}{ccccc} & H & & Cl & \\ & | & & | & \\ H- & C & - & C & -Cl \\ & | & & | & \\ & H & & H & \end{array}$$

1, 1-dichloroethane

or (geminal or gem-dichloroethane)
or (ethylidene chloride)



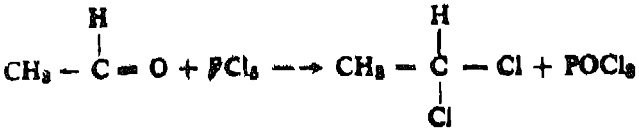
$$\begin{array}{ccccc} & Cl & & Cl & \\ & | & & | & \\ H- & C & - & C & -H \\ & | & & | & \\ & H & & H & \end{array}$$

1, 2-dichloroethane

or (vicinal or vic-dichloroethane)
or (ethylene chloride)

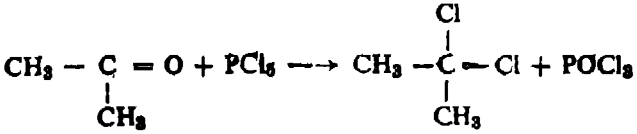
The disubstituted halogen compounds with both substituents attached to the same carbon of the hydrocarbon chain are also known as alkylidene halides. This position of substituents is also known as *geminal* position. Thus 1, 1-dichloroethane is also known as gem –dichloroethane and ethylidene chloride. When the two halogen atoms are attached to the adjacent carbon atoms, this position is called the *vicinal* position and such halides get the name of alkylene halides Accordingly, 1, 2-dichloroethane is also known as vic-dichloroethane and ethylene chloride.

Alkylidene halides can be made by reacting aldehydes or ketones with phosphorus pentahalides.



$$CH_3-\overset{\displaystyle H}{\overset{|}{C}}=O+PCl_5\longrightarrow CH_3-\underset{\displaystyle Cl}{\underset{|}{\overset{\displaystyle H}{\overset{|}{C}}}}-Cl+POCl_3$$

1, 1-dichloroethane



$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}=O+PCl_5\longrightarrow CH_3-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle Cl}{\overset{|}{C}}}}-Cl+POCl_3$$

iso-propylidene chloride or 2,2-dichloropropane

They can also be made by adding hydrogen halides to acetylenes.

$$\mathrm{CH \equiv CH + HX \rightarrow \underset{\text{vinyl halide}}{CH_2 = CHX} \xrightarrow{+HX} \underset{\text{ethylidene halide}}{CH_3 - CHX_2}}$$

Alkylene halides are made by adding halogen to olefins.

$$\mathrm{CH_2 = CH_2 + Cl_2 \longrightarrow \underset{\text{ethylene chloride}}{CH_2Cl - CH_2Cl}}$$

$$\mathrm{CH_3 - CH = CH_2 + Br_2 \longrightarrow \underset{\text{propylene bromide}}{CH_3 - CHBr - CH_2Br}}$$

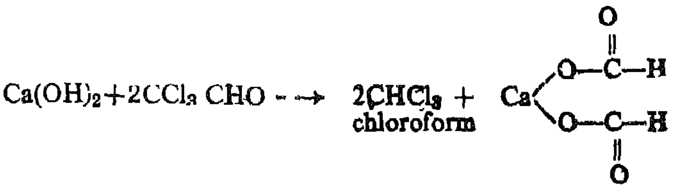
Ethylene chloride boils at 357K and ethylidene chloride boils at 330K. The former on hydrolysis gives the dihydric alcohol, glycol and the latter on hydrolysis gives the unstable 1, 1-dihydroxyethane with the two OH groups attached to the same carbon atom. All such compounds lose a molecule of water and in this case the product of hydrolysis is found to be acetaldehyde, $\mathrm{CH_3CHO}$

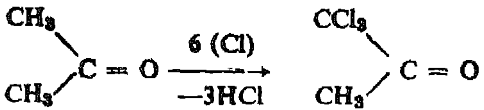
16.8-2 HALOFORMS

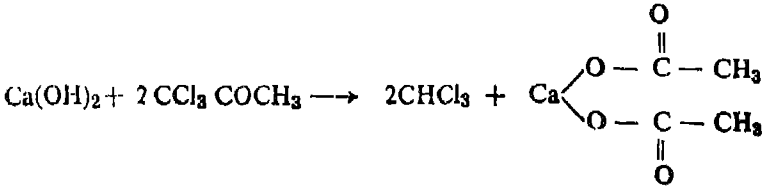
These are trihalogen derivatives of methane. $\mathrm{CHCl_3}$ is called *chloroform* $\mathrm{CHBr_3}$, is called *bromoform* and $\mathrm{CHI_3}$, *iodoform*.

Chloroform is prepared from ethyl alcohol or acetone by the action of chlorine and an alkali or by distillation with bleaching powder. These reagents serve the triple purpose of oxidizing, chlorinating and hydrolysing agents. The complex reactions may be represented by the following stoichiometric steps.

$$\underset{\text{ethanol}}{\mathrm{CH_3CH_2OH}} \xrightarrow[-\mathrm{H_2O}]{(\mathrm{O})} \underset{\substack{\text{acetal-}\\ \text{dehyde}}}{\mathrm{CH_3CHO}} \xrightarrow[-3\mathrm{HCl}]{6\,(\mathrm{Cl})} \underset{\text{chloral}}{\mathrm{CCl_3CHO}}$$

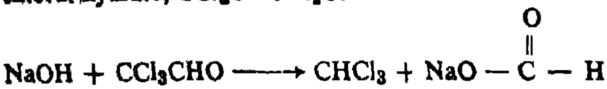






$$Ca(OH)_2 + 2\,CCl_3COCH_3 \longrightarrow 2CHCl_3 + Ca(OCOCH_3)_2$$

Reactions in presence of NaOH and chlorine can be similarly stated. For getting anaesthetic quality of pure chloroform, chloral is first separately prepared and then distilled with aqueous NaOH solution. Chloral is stored in an hydrated form as chloral hydrate, $CCl_3CHO.H_2O$.



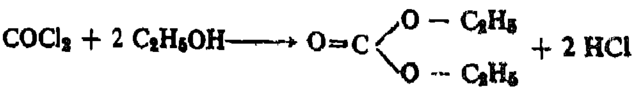
$$NaOH + CCl_3CHO \longrightarrow CHCl_3 + NaO-\overset{\overset{\displaystyle O}{\|}}{C}-H$$

Chloroform is a heavy, colourless, volatile liquid (b.p., 334K) with sweetish odour and taste. It is slightly soluble in water. It is a good solvent for oils, fats, waxes and resins. Inhalation of chloroform vapour induces unconsciousness. It is difficult to burn.

It is slowly oxidized by air in presence of light to the poisonous substance, phosgene or carbonyl chloride, $COCl_2$.

$$2CHCl_3 + O_2 \xrightarrow{\text{light}} 2COCl_2 + 2HCl$$

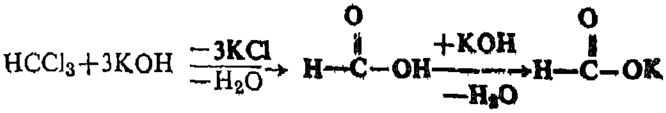
This reaction can be largely prevented by keeping chloroform in brown bottles, completely filled so that air is kept out. Mixing a little ethanol with chloroform checks formation of $COCl_2$ and fixes it as non-volatile ethyl carbonate.



$$COCl_2 + 2\,C_2H_5OH \longrightarrow O{=}C(O-C_2H_5)_2 + 2\,HCl$$

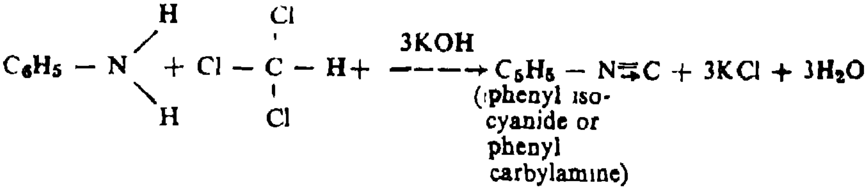
Chloroform to be used as anaesthetic should not give a precipitate with $AgNO_3$ solution.

Chloroform and other haloforms can be hydrolysed by boiling with concentrated aqueous or ethanolic solutions of alkalies :



$$HCCl_3 + 3KOH \xrightarrow[-H_2O]{-3KCl} H-\overset{\overset{\displaystyle O}{\|}}{C}-OH \xrightarrow[-H_2O]{+KOH} H-\overset{\overset{\displaystyle O}{\|}}{C}-OK$$

Warming chloroform with any primary amine in presence of alcoholic potash yields an offensive smelling *isocyanide* or *carbylamine*. This reaction is known as carbylamine test for primary amines and chloroform. Other haloforms react in a similar way. Aniline is usually taken as the primary amine for reactions with haloforms.



$$C_6H_5-NH_2 + Cl-CCl_2-H \xrightarrow{3KOH} C_6H_5-N\equiv C + 3KCl + 3H_2O$$

(phenyl isocyanide or phenyl carbylamine)

Haloforms, when heated with silver powder, lose the halogen atoms and form acetylene.

$$2\,CHX_3 + 6\,Ag \longrightarrow CH \equiv CH + 6\,AgCl$$

Iodoform test : Formation of iodoform is used as a test for ethanol, acetaldehyde and all such ketones which have a methyl group linked to the carbonyl group. Methanol does not give this test. The test is carried out by warming to 333K the substance to be tested with aqueous solutions of sodium carbonate (mild alkali) and iodine. Yellow crystalline precipitate of iodoform which can be easily recognized by its form and odour, will be formed if any of the substances listed above be present. The reaction for iodoform may be written in the same way as mentioned for chloroform :

$$RCOCH_3 + 3I_2 + 4NaOH \longrightarrow CHI_3 + RCOONa + 3\,NaI + 3H_2O$$

16.8.3. SOME CHLORO SOLVENTS AND INSECTICIDES

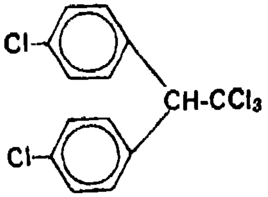
Carbon tetrachloride or tetrachloromethane (CCl_4) is a commercially important solvent. Its boiling point is 350K It is practically insoluble in water and is a good solvent for most organic substances Its vapour is heavy, non-inflamable and stable. It is used as fire extinguisher under the name *pyrene*. In contact with fire it can form poisonous substance, phosgene ($COCl_2$). Thus care needs to be taken when pyrene is used for extinguishing fires.

Westron or acetylene tetrachloride, $CHCl_2\,CHCl_2$, is a heavy non-inflammable liquid, boiling at 419K It is a good solvent for oils, paints, varnishes, rubber, etc.

Westrosol or trichloroethylene, $CHCl = CCl_2$, is a better solvent than westron and has a lower boiling point of 363K. It is useful in dry-cleaning of clothes

Freon or dichlorodifluoromethane, CCl_2F_2, is a non-toxic, non-inflammable, easily liquefiable gas, used as a refrigerant and as propellent in aerosols and foams.

DDT is an important commercial insecticide It is 2,2-bis-(*p*-chlorophenyl) -1,1,1-trichloroethane.



DDT

It was given the trade name DDT on the basis of its initial (though erroneous) name dichlorodiphenyl trichloroethane.

BHC, benzene hexachloride or hexachlorocyclohexane, $C_6H_6Cl_6$ is an important agricultural pesticide, chiefly used for exterminating termite white ants) from soil. It occurs in a number of stereoisomers. Only the γ (gamma)-isomer has good insecticidal action. It also goes by the trade names of *gammexane*, *lindane* and 666. Hexachlorobenzene, C_6Cl_6, is insoluble in water and a much poorer insecticide.

Chlordane or chlordom is another chloroinsecticide It is chlorinated hexahydromethanoindene.

One should be very careful in using these insecticides as they are also poisonous for human beings and animals and what is worse is that they are accumulated in our bodies and eventually produce unremediable harms.

16.9 HALOGEN DETECTION

Presence of a halogen in an organic compound can be detected in a number of ways A halogen atom linked to a single bonded carbon atom which is linked to other carbon atoms in the molecule by single bonds, easily reacts with reagents like aqueous and alcoholic alkalies, ammonia and ethoxide to form water soluble halides. These can be detected with $AgNO_3$. An alcoholic solution of $AgNO_3$ gives a precipitate of silver halides on warming in such cases.

When the halogen is present on a carbon atom bonded, to another carbon atom by a double bond, it will not easily react with the above mentioned reagents.

However, all halogen derivatives react with fused metallic sodium forming sodium halides (Part I, Sec 19.2).

EXERCISES

16.1 Explain the following terms:

(a) optical activity,
(b) specific rotation,
(c) plane of symmetry,
(d) resolution,
(e) racemic modification,
(f) polarimeter,
(g) mirror plane,
(h) racemisation,
(i) configuration,
(j) monochromatic light,
(k) meso isomer,
(l) polarised light

16.2 Which of the following are optically active compounds:

(a) n-butanol,
(b) 4-hydroxy heptane,
(c) 2-chlorobutane, and
(d) 3-chloropentane.

16.3 Explain the following.

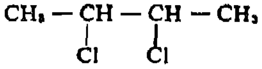
(a) The physical properties of geometric isomers are different while those of optical isomers are the same.

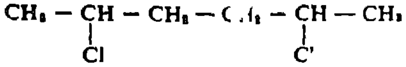
(b) Allyl chloride $[CH_2=CH-CH_2Cl]$ is hydrolysed more readily than propylchloride.

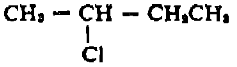
(c) The boiling point of ethyl bromide is higher than that of ethyl chloride.

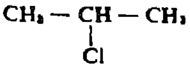
(d) The treatment of an alkyl chloride with aq. KOH leads to the formation of alcohols whereas in the presence of alcoholic KOH alkenes are the major products.

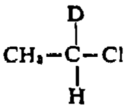
16.4 How many optically active isomers are possible for each of the following

(a) 
$CH_3-\underset{Cl}{CH}-\underset{Cl}{CH}-CH_3$

(b) 
$CH_3-\underset{Cl}{CH}-CH_2-CH_2-\underset{Cl}{CH}-CH_3$

(c) 
$CH_3-\underset{Cl}{CH}-CH_2CH_3$

(d) 
$CH_3-\underset{Cl}{CH}-CH_3$

(e) 
$CH_3-\overset{D}{\underset{H}{C}}-Cl$

16.5 Write all the possible structures for a compound with a molecular formula C_4H_9Br. Name these according to IUPAC nomenclature. How many optically active isomers are possible?

16.6 Discuss four methods for the preparation of alkyl chlorides? Give one reason why the organic halogen compounds used as solvents in industry are chlorides rather than bromides.

16.7 How will you convert

(a) benzene ⟶ m-nitrochlorobenzene

(b) benzene ⟶ o-nitrochlorobenzene

(c) toluene ⟶ benzyl chloride

(d) 2-propanol ⟶ 1-bromopropane

(e) n-proponol ⟶ 1-nitropropane

(f) 2-methyl-1-propene ⟶ 2-chloro-2-methyl propane

(g) ethyl chloride ⟶ ethyl amine

(h) n-propyl bromide ⟶ iso-propyl bromide

16.8 How will you distinguish between (give chemical tests)

(a) C_6H_5Cl and $C_6H_{11}Cl$

(b) $CH_3CH_2CH_2Br$ and $CH_2 = CH-CH_2Br$

(c) C_6H_5Cl and $C_6H_5CH_2Cl$

(d) $C_6H_5CH_2Cl$ and $C_6H_5CH_2Br$

16.9 How will you convert 2-chlorobutane into :

(a) *sec* butyl ethyl ether

(b) 2 butanol

(c) 2-butene

(d) 2-aminobutane

(e) 2-nitrobutane

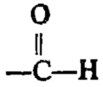
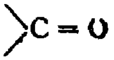
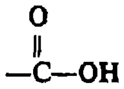
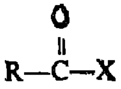
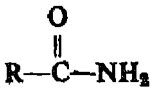
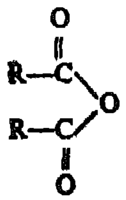
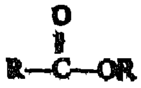
(f) n-butane

(g) 3, 4-dimethyl hexane

UNIT 17

Compounds with Functional Groups Containing Oxygen

The compounds with oxygen containing functional groups are:

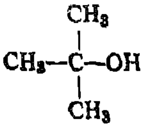
Alcohols and phenols	—OH
Ethers	—O—
Aldehydes	 $-\overset{\overset{\displaystyle O}{\|}}{C}-H$
Ketones	
Carboxylic acids	 $-\overset{\overset{\displaystyle O}{\|}}{C}-OH$
Derivatives of acids	
Acid or acyl halides	 $R-\overset{\overset{\displaystyle O}{\|}}{C}-X$
Acid amides	 $R-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2$
Acid anhydrides	
Esters	 $R-\overset{\overset{\displaystyle O}{\|}}{C}-OR$

17.1 ALCOHOLS AND PHENOLS

Alcohols and phenols are the compounds in which one or more hydroxyl groups (—OH) are present as functional groups. In an alcohol the—OH group is attached to an alkyl group and in a phenol it is attached to an aromatic ring.

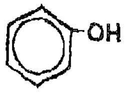
CH_3CH_2OH

ethyl alcohol

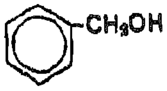


$CH_3—C(CH_3)_2—OH$

tert-butyl alcohol

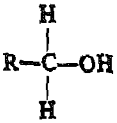


phenol



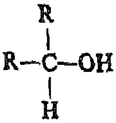
benzyl alcohol

Alcohols having one OH group per molecule are called monohydric alcohols*. We are already familiar with the classification of carbon atoms in a chain as primary, secondary and tertiary carbons based on the number of other carbon atoms attached to them (Part I). Alcohols are also classified as primary, secondary or tertiary alcohols depending upon the type of carbon carrying the OH group.



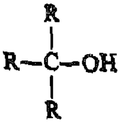
$R—CH_2—OH$

primary
alcohol



$R—CHR—OH$

secondary
alcohol

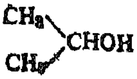


$R—CR_2—OH$

tertiary
alcohol

17.1.1 NOMENCLATURE

The trivial and IUPAC names of the first few members of alcohols series are as follows :

Molecular formula	*Trivial name*	*IUPAC name*
CH_3OH	methyl alcohol	methanol
CH_3CH_2OH	ethyl alcohol	ethanol
$CH_3CH_2CH_2OH$	*n*-propyl alcohol	1-propanol
	*iso*-propyl alcohol	2-propanol

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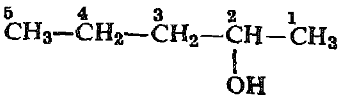
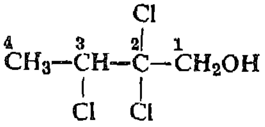
*Compounds with more than one hydroxyl groups per molecule are discussed in the Unit-19 on polyfunctional compounds.

In IUPAC nomenclature 'e' of the corresponding alkane is replaced by 'ol' and a numerical prefix is used to indicate the position of OH group on the carbon chain. Since OH is the functional group, the largest carbon chain involving this group is selected as the parent chain and the numbering is done in such a way that the carbon with the OH group gets the lowest possible number.



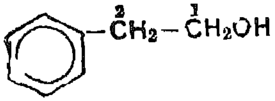
$\overset{5}{C}H_3-\overset{4}{C}H_2-\overset{3}{C}H_2-\underset{OH}{\overset{2}{C}H}-\overset{1}{C}H_3$

2-pentanol

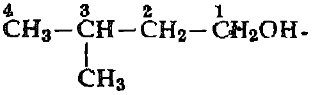


$\overset{4}{C}H_3-\underset{Cl}{\overset{3}{C}H}-\underset{Cl}{\overset{Cl}{\overset{2}{C}}}-\overset{1}{C}H_2OH$

2, 2, 3-trichlorobutanol



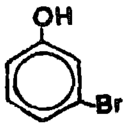
2-phenyl ethanol



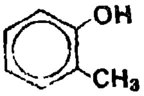
$\overset{4}{C}H_3-\underset{CH_3}{\overset{3}{C}H}-\overset{2}{C}H_2-\overset{1}{C}H_2OH$

3-methyl butanol

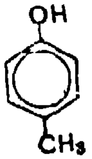
Substituted phenols are named as the derivatives of simplest aromatic hydroxy compound phenol. Methyl phenols are called cresols.



m-bromophenol



o-cresol



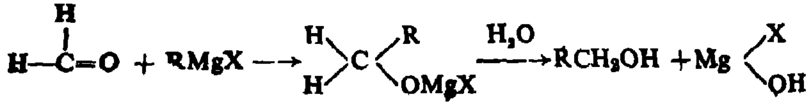
p-cresol

17.1-2 LABORATORY PREPARATION

A. ALCOHOLS

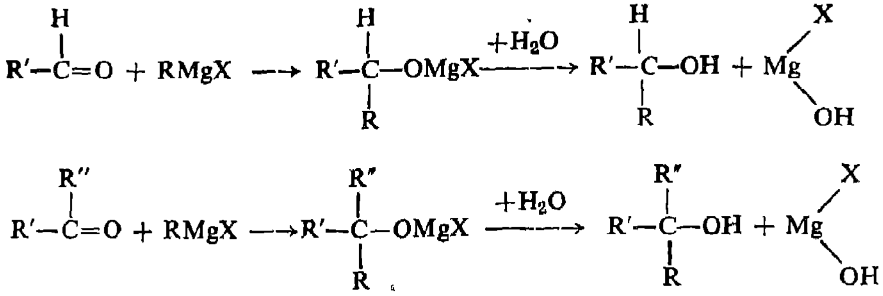
1. From aldehyde and ketones

(a) ***By Grignard reagents*** : Grignard reagents react with aldehydes and ketones to give secondary and tertiary alcohols respectively. Formaldehyde gives primary alcohols.

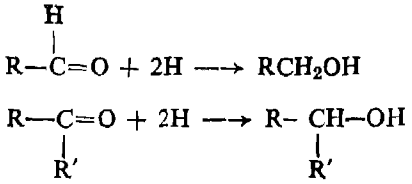


$$H-\overset{H}{\overset{|}{C}}=O + RMgX \longrightarrow \begin{matrix}H\\H\end{matrix}\!>C<\!\begin{matrix}R\\OMgX\end{matrix} \xrightarrow{H_2O} RCH_2OH + Mg<\begin{matrix}X\\OH\end{matrix}$$

Thus ethyl alcohol will be formed by reacting formaldehyde with CH_3-Mg-X



(b) *By reduction of aldehydes and ketones* : Aldehydes are reduced to primary alcohols whereas ketones are reduced to secondary alcohols. The normal reducing agents used are $LiAlH_4$ and H_2 in presence of a catalyst (Ni, Pt or Pd).



$$R-\overset{\displaystyle H \atop |}{C}=O + 2H \longrightarrow RCH_2OH$$

$$R-\underset{| \atop \displaystyle R'}{C}=O + 2H \longrightarrow R-\underset{| \atop \displaystyle R'}{C}H-OH$$

2. By hydrolysis of alkyl halides

We have already studied that alkyl halides are hydrolyzed by aqueous alkalies to the corresponding alcohols

$$RX + OH^- \longrightarrow ROH + X^-$$

B PHENOLS

Phenols are prepared in the laboratory by the hydrolysis of diazonium salts.

$$Ar\,N_2^+X^- + H_2O \xrightarrow{\text{warming}} ArOH + N_2 + HX$$

We will study more about this reaction under amines (Unit 18)

Industrial Preparations

There are two main industrial sources for alcohols

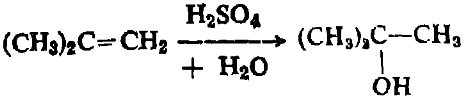
(i) Hydration of alkenes

(ii) Fermentation of carbohydrates

(i) *Hydration of alkenes* : We have already studied that alkenes can be obtained by cracking of petroleum and can be separated from the mixture by fractionation.

These can be readily converted into alcohols by the addition of water in the presence of sulphuric racid.

$$CH_2{=}CH_2 \xrightarrow[+\ H_2O]{H_2SO_4} CH_3CH_2OH$$



$$(CH_3)_2C{=}CH_2 \xrightarrow[+\ H_2O]{H_2SO_4} (CH_3)_3\underset{\displaystyle OH}{\underset{|}{C}}{-}CH_3$$

(*ii*) *Fermentation of carbohydrates* : The oldest method for the manufacture of ethyl alcohol is fermentation* of sugars by yeast** The industrial sources for sugar are molasses, sugar rich fruit juices and starch (from potatoes, maize barley, etc.),

From Sugar

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{Invertase}^{***}} \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

$$\underset{\substack{\text{glucose}\\ \text{or}\\ \text{fructose}}}{C_6H_{12}O_6} \xrightarrow{\text{Zymase}^{***}} 2C_2H_5OH + 2CO_2$$

From Starch :

$$2\ (C_6H_{10}O_5)n + nH_2O \xrightarrow{\text{Diastase}} \underset{\text{maltose}}{nC_{12}H_{22}O_{11}}$$

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{Maltase}^{***}} \underset{\text{glucose}}{2C_6H_{12}O_6}$$

$$C_6H_{12}O_6 \xrightarrow{\text{Zymase}^{***}} 2C_2H_5OH + 2\ CO_2$$

In addition to ethyl alcohol, a small amount of fusel oil (mixture of mostly higher primary alcohols) is also obtained when starch is fermented.

---

* **Fermentation : Degradation of organic compounds into simpler compounds with the help of enzymes.**

** **Yeast is a source of different enzymes.**

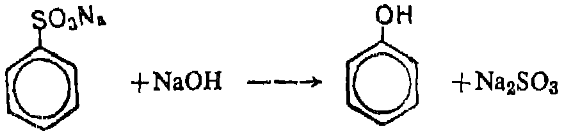
*** ***Enzymes***

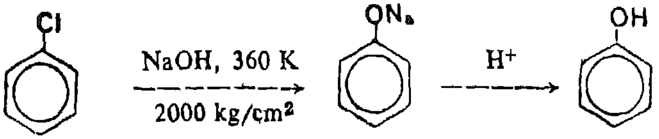
(Enzymes are complex organic compounds which catalyze specific chemical reactions taking place in living organism. Invertase, zymase, diastase, maltase are examples of enzymes).

Methanol is obtained as a by-product by the destructive distillation of wood during the manufacture of charcoal. Methanol is also manufactured by passing a mixture of carbon monoxide and hydrogen over Cr_2O_3 ZnO at 673K.

$$CO + 2H_2 \xrightarrow[Cr_2O_3.ZnO]{623\text{-}673K} CH_3OH$$

Phenols and cresols are obtained from the middle fraction 443-503K obtained by coal tar distillation. Synthetically phenol is manufactured by the fusion of sodium benzene sulphonate with alkali and the reaction of chlorobenzene with aqueous sodium hydroxide under high temperature and pressure conditions (Dow process)





17.1-3 PHYSICAL PROPERTIES

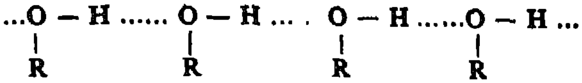
The physical properties of alcohols may be considered as a combined effect of the presence of non-polar hydrocarbon part and the polar hydroxyl group in the molecule.

The boiling points of alcohols increase with an increase in molecular mass In isomeric alcohols increased branching in the hydrocarbon part reduces the boiling point. This trend is similar to that in alkanes, (Part I)

The most prominent property of hydroxy compounds is association of their molecules through hydrogen bonding. Alcohols have higher boiling points than the corresponding hydrocarbons and alkyl halides. For example, methyl alcohol has a much higher b. p. as compared to methyl halides and methane.

Compounds	CH_4	CH_3Cl	CH_3Br	CH_3OH
b p. (K)	111	249	278	337.5.

The reason for this difference lies in the much higher polarity of the — OH group. This results in strong hydrogen bonding amongst alcohol molecules (compare with H_2O, b. p. 373 K).



$$\cdots\underset{\displaystyle R}{\underset{|}{O}}-H\cdots\cdots\underset{\displaystyle R}{\underset{|}{O}}-H\cdots\;\underset{\displaystyle R}{\underset{|}{O}}-H\cdots\cdots\underset{\displaystyle R}{\underset{|}{O}}-H\cdots$$

It takes quite a larg amount of energy to break the extensive hydrogen bonds which hold so many alcohol molecules together. Consequently the boiling points of alcohols are significantly higher than the corresponding hydrocarbons

Solubility of an alcohol in water depends upon the capacity of its molecules to form hydrogen bonds with water molecules. Both in alcohols and in water, the molecules are held together by inter-molecular forces of similar kind The energy required to break association between two alcohol molecules or between two water molecules is provided by the hydrogen bond formations between a water and an alcohol molecule. Alcohols of lower molecular masses are completely miscible with water The hydrocarbon part of an alcohol molecule resists entering into water and when the hydrocarbon part becomes larger, the solubility effect of OH group is outweighed by the large repulsive effect of non-polar portion of alcohol and then the alcohol becomes insoluble in water. Thus solubility of alcohols in water decreases with the lengthening of the hydrocarbon chain.

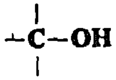
Phenols also have higher boiling points than aromatic hydrocarbons because of intermolecular hydrogen bonding. Most phenols are sparingly soluble in water because of the larger hydrocarbon part in the molecule (only 9g of phenol dissolves in 100g of water).

17.1-4 CHEMICAL REACTIONS OF ALCOHOLS AND PHENOLS

Chemical reactions of alcohols (R—OH) are of two types .

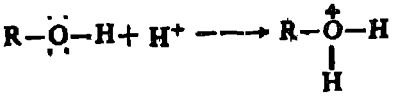
(1) Involving cleavage of carbon-oxygen bond (C$\div$OH) with removal or substitution of OH group, and (2) Involving cleavage of oxygen-hydrogen bond CO$\div$H) with removal or substitution of hydrogen atom.

(1) Cleavage of carbon-oxygen bond



$$-\overset{|}{\underset{|}{C}}-OH$$

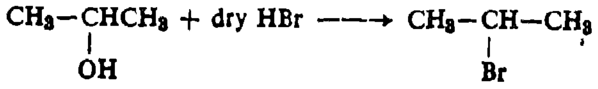
(i) *Reactions with mineral acids like H_2SO_4, HBr, HCl, etc.* : Because of the lone pairs of electrons on the oxygen atom, alcohols behave as weak bases In the presence of strong mineral acids, they undergo protonation to give positively charged



$$R-\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}-H+H^{+}\longrightarrow R-\underset{\displaystyle H}{\underset{|}{\overset{+}{O}}}-H$$

oxonium ions in which the positive charge on the oxygen atom considerably weakens the C—O bond. Neutral H_2O being good leaving group (unlike OH^-), facilitates various reactions in which the —OH group gets replaced.

We have seen in the preparation of alkyl halides that alcohols readily react with hydrogen halides to give alkyl halides and water. This reaction is normally carried out by passing dry hydrogen halides into heated alcohol or by heating the alcohol with concentrated hydrogen halide solution.



$$CH_3-\underset{OH}{\underset{|}{C}}HCH_3 + \text{dry HBr} \longrightarrow CH_3-\underset{Br}{\underset{|}{C}}H-CH_3$$

$$(CH_3)_3C-OH + HCl \longrightarrow (CH_3)_3C-Cl$$

Anhydrous zinc chloride or some other suitable dehydrating agent may be added to absorb water formed in the reaction and to enable the reaction to go to completion.

$$CH_3CH_2OH + HCl \xrightarrow[\text{Heat, }ZnCl_2]{-H_2O} CH_3CH_2Cl$$

Tertiary alcohols are found to be most reactive in such reactions; they are followed by secondary alcohols and reactivity of primary alcohols is the least

The order of reactivity of various halogen acids is HI>HBr>HCl. This is because I^- is a better nucleopile than Br^- which in turn is better than Cl^-.

The acidic nature of phenolic-OH group makes protonation of oxygen less feasible. So the phenols do not undergo reactions involving substitution of OH groups like alcohols.

(ii) *Dehydration of alcohols:* When ethanol and higher alcohols are heated above 423 K with concentrated mineral acids, especially H_2SO_4, they undrgo dehydration to form olefins.

$$C_2H_5OH \xrightarrow[-H_2O]{H_2SO_4,\ 443\ K} CH_2 = CH_2$$

In these reactions also, first protonation of alcohol takes place. This is followed by loss of water and proton from adjacent carbon atom.

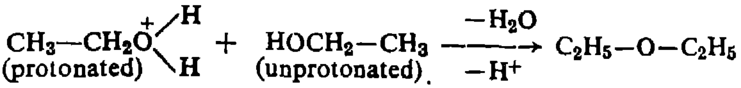
The ease of dehydration of alcohols is in the order

tertiary > secondary > primary

If less than one equivalent of sulphuric acid is used, and the temperature is kept below 423K many alcohols can be converted into corresponding ethers by loss of a water molecule from two molecules of the alcohol.

$$C_2H_5OH + HOC_2H_5 \xrightarrow[-H_2O]{H_2SO_4,\ 413\ K} \underset{\text{diethyl ether}}{C_2H_5OC_2H_5}$$

By using less than one equivalent of mineral acid, some alcohol molecules remain unprotonated and these can lead to loss of water from the protonated alcohol molecules.



$$\underset{\text{(protonated)}}{CH_3-CH_2\overset{+}{O}H_2} + \underset{\text{(unprotonated)}}{HOCH_2-CH_3} \xrightarrow[-H^+]{-H_2O} C_2H_5-O-C_2H_5$$

If the temperature is raised beyond 423 K, olefin is formed Lewis acids like Al_2O_3 can be used in place of mineral acids both for dehydration of alcohols to *alkenes* and preparation of ethers.

(iii) *Reaction with PX_3*: Alcohols are easily converted into the corresponding halides by reaction with phosphorus trihalides (PX_3) or thionyl halides (SOX_2).

$$3\ CH_3CH_2OH + PBr_3 \longrightarrow 3\ CH_3CH_2Br + H_3PO_3$$

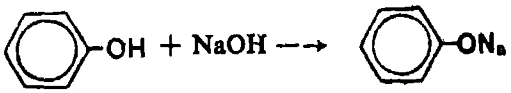
$$CH_3CH_2OH + SOCl_2 \longrightarrow CH_3CH_2Cl + SO_2 + HCl$$

(2) Cleavage of oxygen-hydrogen bond

(*i*) *Acid-base character*: We have seen above that alcohols behave as bases and get protonated by strong acids. They can also act as weak acids and as such undergo a replacement of hydrogen of the highly polar oxygen-hydrogen bond by some more electropositive elements to form alkoxides, RO^-M^+.

$$ROH + Na \longrightarrow RO^-Na^+ + \tfrac{1}{2}H_2$$

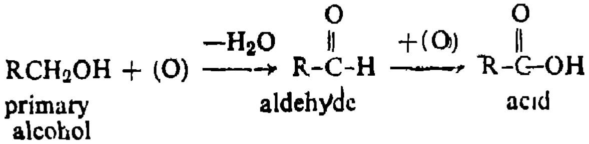
The order of acidity of various alcohols is primary > secondary > tertiary. Wit the increase in the number of alkyl groups as we go from primary to secondary t tertiary alcohol, it becomes more difficult for the OH hydrogen to be replaced b electropositive elements. Phenols are much more acidic than alcohols and easil react with sodium or potassium hydroxide to form salts. These salts are solubl in water.



sodium phenoxide.

The dissociation constants, K_a (as acids) for alcohol, water and phenol are 1×10^{-1} 1×10^{-14} and 1.02×10^{-10} respectively. Water being a stronger acid than alcoho decomposes alkoxides to give back alcohols and metals hydroxides. Phenoxide regenerate phenol only on treatment with acids stronger than phenols.

(ii) *Oxidation of alcohols*: The product of oxidation of an alcohol depend upon the number of hydrogens present on the carbon carrying the OH oroup. A room temperature primary alcohols are oxidized to carboxylic acids by the common oxidizing agents like potassium permanganate or acidified potassium dichromate. Aldehydes are formed as intermediate products

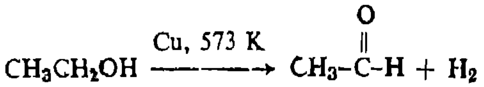


$$RCH_2OH + (O) \xrightarrow{-H_2O} \underset{\text{aldehyde}}{R{-}\overset{\overset{O}{\|}}{C}{-}H} \xrightarrow{+(O)} \underset{\text{acid}}{R{-}\overset{\overset{O}{\|}}{C}{-}OH}$$

primary alcohol

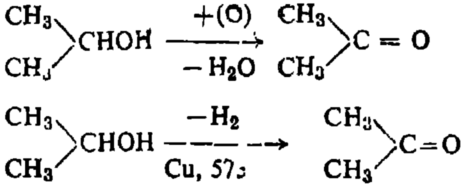
Aldehydes are lower boiling and acids are higher boiling than the original alcohols. By running the oxidation at a temperature below the boiling point of alcohol and above that of aldehyde, it is possible to distil off the aldehyde from the reaction mixture.

Another method of getting aldehydes from primary alcohols is dehydrogenation process which is usually carried out by passing alcohol vapour over copper heated to 573 K.



$$CH_3CH_2OH \xrightarrow{Cu,\ 573\ K} CH_3{-}\overset{\overset{O}{\|}}{C}{-}H + H_2$$

Secondary alcohols on oxidation give ketones and these are resistant to further oxidation under less drastic conditions. The ketones can also be prepared by the dehydrogenation process.



$$(CH_3)_2CHOH \xrightarrow[-H_2O]{+(O)} (CH_3)_2C=O$$

$$(CH_3)_2CHOH \xrightarrow[Cu,\ 573]{-H_2} (CH_3)_2C=O$$

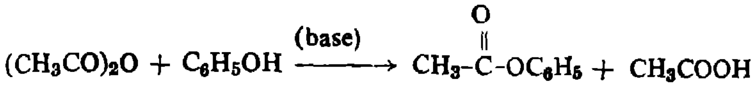
In tertiary alcohols there is no hydrogen on the carbon carrying the OH group. Consequently, tertiary alcohols resist oxidation and undergo instead a dehydration reaction to give alkenes. The alkene formed may get further oxidized.

(iii) *Ester formation :* Alcohols and phenols react with carboxylic acids to form esters. The reaction needs to be catalyzed by strong acids and dehydrating agents. It is otherwise a reversible reaction.

$$ROH + R'COOH \overset{H}{\rightleftharpoons} RCOOR' + H_2O$$

In the laboratory, esters can be conveniently prepared by the reaction of acid chlorides or acid anhydrides with alcohols or phenols in the presence of a base such as pyridine. The base removes the acid which is formed as a product of reaction.

$$C_6H_5OH + C_6H_5COCl \xrightarrow{\text{(base)}} C_6H_5COOC_6H_5 + HCl$$



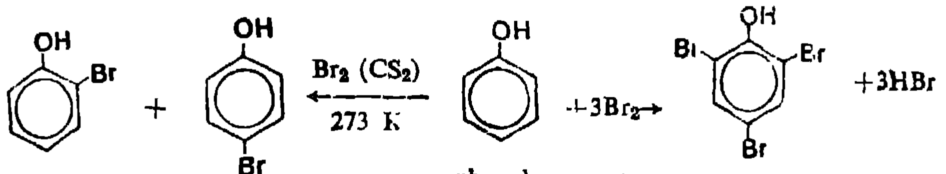
$$(CH_3CO)_2O + C_6H_5OH \xrightarrow{\text{(base)}} CH_3\text{-}\overset{O}{\overset{\|}{C}}\text{-}OC_6H_5 + CH_3COOH$$

We shall learn more about this reaction in a later section

Ring Substitution in Phenol

We know that OH group is an ortho/para directing group (Part I of this book). Phenols readily undergo substitution giving mixture of ortho and para substitution products.

(i) *Bromination:* Phenol is readily converted into 2, 4, 6-tribromophenol on treatment with bromine water.

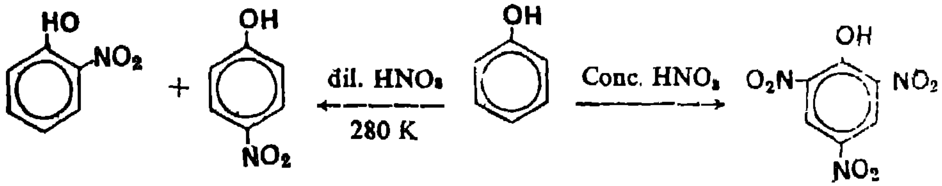


phenol 2, 4, 6-tribromophenol

o-bromophenol *p*-bromophenol

Monobromophenols can be obtained by carrying out the substitution in presence of less polar solvents like CS_2 and at low temperature.

(ii) *Nitration:* Nitration of phenol with concentrated nitric acid gives 2, 4 6-trinitrophenol (picric acid) * Nitration at low temperatures using dilute nitric acid yields a mononitration product.



o-nitrophenol *p*-nitrophenol phenol 2,4,6-trinitrophenol

(iii) *Kolbe's reaction*. When sodium phenoxide is heated with carbon dioxide at 400K under a pressure of 4 to 7 atmospheres and the product is acidified, we get o-hydroxy benzoic acid, known as salicylic acid. This reaction is called Kolbe's reaction. A small amount of p-hydroxy benzoic acid is also formed.

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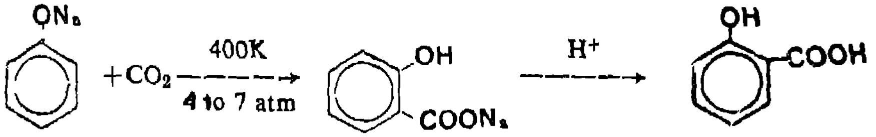
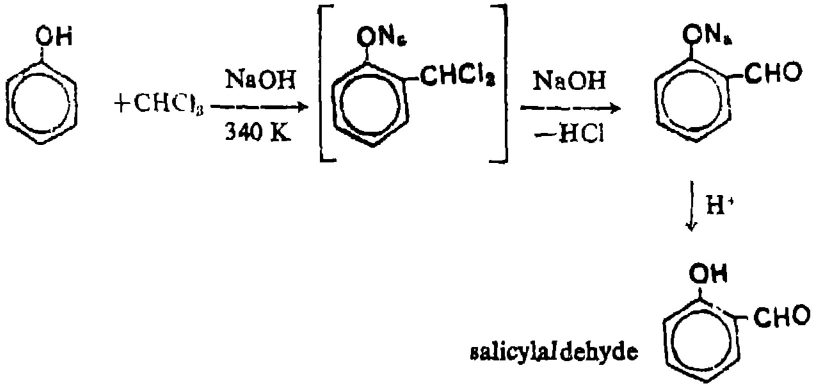
* Picric acid explodes on detonation in the dry state and is used as a high explosive in shell bombs and torpedoes and is kept under water.



sodium salicylate salicylic acid

(iv) *Reimer-Tiemann reaction* : Treatment of phenol with chloroform in the presence of aqueous alkali at 340K followed by hydrolysis of the resulting product gives o-hydroxy benzaldehyde (salicylaldehyde). This reaction is known as Reimer-Tiemann reaction.



salicylaldehyde

17.1-5 METHODS FOR DIFFERENTIATING PRIMARY, SECONDARY AND TERTIARY ALCOHOLS

(i) *Oxidation Test :* A primary alcohol on oxidation gives an aldehyde which gets further oxidized to a carboxylic acid, each having the same number of carbons as the original alcohol. A secondary alcohol on oxidation is converted into a ketone containing the same number of carbons. It does not undergo further oxidation. Only under drastic conditions a ketone may be oxidized further to a mixture of carboxylic acids each containing a lesser number of carbon atoms than the original alcohol. A tertiary alcohol is not oxidized under normal conditions. If acid be present, it gets dehydrated to an olefin which may be further oxidized.

(ii) *Lucas Test :* This test is based on the difference in reactivity of primary, secondary and tertiary alcohols towards hydrochloric acid. It involves the treatment of the alcohol with the *Lucas reagent*, which is a solution of zinc chloride in concentrated hydrochloric acid. The alcohol reacts with the reagent to give the corresponding alkyl chloride. However, we know that lower alcohols (upto six carbon atoms) are soluble in water and the corresponding alkyl chlorides are insoluble in water. The formation of an alkyl chloride is detected by the appearance of a separate layer or cloudiness. Tertiary alcohols react immediately, secondary alcohols take a few minutes time to give cloudiness Primary alcohols do not react at all at room temperatures and hence no cloudiness is observed in their case

17.1-6 TESTS FOR PHENOLS

Phenols are stronger acids than water but weaker acids than carboxylic acids Thus a water insoluble compound that dissolves in aqueous sodium hydroxide but not in aqueous sodium bicarbonate is most likly a phenol. Phenols also form coloured complexes (usually blue, violet and green) with neutral ferric chloride.

17.1-7 ABSOLUTE ALCOHOL

Fractional distillation of an aqueous solution of ethyl alcohol yields rectified spirit containing a maximum of about 95% ethanol. As the vapour obtained from it on distillation has the same composition as the liquid itself, it is not possible to get more concentrated alcohol by further fractionation In order to get 100 per cent ethanol (known as *absolute alcohol*) rectified spirit is mixed with some benzene and the mixture is subjected afresh to fractional distillation A mixture containing all the water, some alcohol and some benzene distils out first at about 338 K Remaining benzene and some more alcohol distils over next at a slightly higher temperature. Pure alcohol is left as a residue and distils, the last.

17.1-8 INDUSTRIAL ALCOHOL

The manufacture and sale of alcohol is under Government's control because of its use in beverages like beer, whisky, brandy, etc. Use of alcohol for beverages is highly taxed.

Ethyl alcohol is also very important for various chemical industries and is taxed at much lower rates for these industries The solvent alcohol for industries is available after mixing with poisonous substances like methanol, rubber distillates and gasoline This makes it unfit for drinking purposes and is sold under the name of *denatured alcohol* or *methylated spirit.* Some ethanol is also mixed with petrol hydrocarbons for use as fuel in automobiles, such alcohol is called *power alcohol*

17.1-9 TOXICITY OF ALCOHOLS

The toxicity of alcohols varies from compound to compound. Thus methyl alcohol is highly toxic and small amounts taken internally may produce blindness or may even be fatal Ethyl alcohol is non-toxic but produces definite physiological effects. It disturbs the brain activity and slows down its functions.

17.1-10 USES OF ALCOHOLS AND PHENOLS

Methanol is largely used as a solvent in the plastics and textile industries It is also used for the production of formaldehyde, for power boosters in gasoline engines and for antifreezes. Commercial airliners burn a carburettor injection mixture of 60% methanol and 40% water which increases power on take-off Ethanol is used as a solvent and as a starting material for synthetic products such as lacquers, varnishes, perfumes and cosmetics, dyes, inks, synthetic rubber, etc.

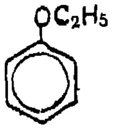
A large fraction of phenol supply goes into the production of bakelite plastics and resins. Phenols are also used in preparing drugs, dyes, perfumes, local anesthetics, etc.

17.2 ETHERS

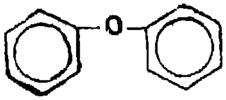
The general formula for ethers is R—O—R′. R and R′ may be alkyl or aryl radicals. If both the groups are the same, the ether is said to be a symmetrical or simple ether and if different, unsymmetrical or mixed ether.

$H_5C_2-O-C_2H_5$

diethyl ether



phenyl ethyl ether



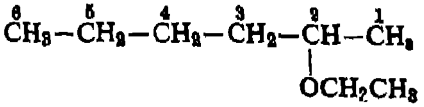
diphenyl ether

17.2-1 NOMENCLATURE

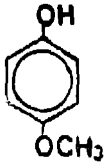
The trivial and IUPAC names of the first few members are given below ·

Molecular formula	*Trivial name*	*IUPAC name*
CH_3-O-CH_3	Dimethyl ether	Methoxymethane
$CH_3-O-C_2H_5$	Methyl ethyl ether	Methoxyethane
$C_2H_5-O-C_2H_5$	Diethyl ether	Ethoxyethane

In the trivial nomenclature, the names of two alkyl groups are written separately and are followed by the word ether. According to IUPAC nomenclature, the simpler of the two alkyl groups is made the alkoxy derivative followed by the alkane from which the other alkyl group is derived and the name is written as one word. If a hydroxyl group is also present in the ether molecule, the compound is considered as the derivative of the alcohol and the ether group is named as an alkoxy substituent



$$\overset{6}{C}H_3-\overset{5}{C}H_2-\overset{4}{C}H_2-\overset{3}{C}H_2-\underset{OCH_2CH_3}{\overset{2}{C}H}-\overset{1}{C}H_3$$



$$CH_3O\overset{2}{C}H_2\overset{1}{C}H_2OH$$

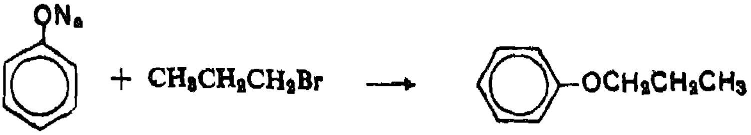
2-ethoxyhexane *p*-methoxyphenol 2-methoxyethanol

17.2-2 LABORATORY PREPARATION OF ETHERS

Ethers are prepared in the laboratory by the reaction of corresponding alkoxides or phenoxides with alkyl halides. This method is known as *Williamsons synthesis of ethers* and may be used for the preparation of symmetrical as well as unsymmetrical ethers

$$RONa + R'X \longrightarrow ROR' + NaX$$

$$CH_3CH_2ONa + CH_3CH_2I \longrightarrow CH_3CH_2OCH_2CH_3$$



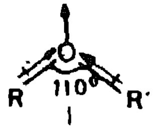
This reaction has its limitations especially with tertiary halides, where the elimination reaction is a competitive reaction due to strongly basic nature of sodium alkoxides.

$$(CH_3)_3CI \xrightarrow[RONa]{-HI} (CH_3)_2C = CH_2$$

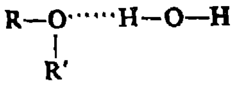
So while planning the synthesis of ethers having a tertiary alkyl group as one of the alkyl groups in R–O–R′, alkoxide from tertiary alcohol is allowed to react with primary halide. For example, to prepare $(CH_3)_3C-O-CH_2CH_3$ we will start with $(CH_3)_3CONa$ and CH_3CH_2Br and not with $(CH_3)_3C\text{-}Br$ and CH_3CH_2ONa. Aryl-alkyl ethers are industrially prepared by Williamsons synthesis.

17.2-3 PHYSICAL PROPERTIES

The carbon-oxygen-carbon (C–O–C) bond angle is about 110°. So the dipole moments of the two C–O bonds do not cancel. Therefore, ethers have some net dipole moments (1.18 D) which is however smaller than for alcohols.



Ethers are weakly polar compounds. Ethers have boiling points nearer to the alkanes of comparable molecular masses than to alcohols. Boiling points of methyl ethyl ether and n-butane are 281K and 268K, respectively. Ethers show nearly the same solubility in water as the isomeric alcohols. Diethyl ether and n-butyl alcohol have nearly the same solubility in water (about 8g per 100g of water). This may be due to some hydrogen bonding possible between water and ether through the oxygen atoms in ether molecules

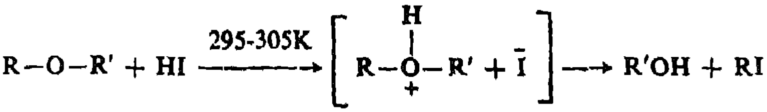

$$R-\underset{\underset{R'}{|}}{O}\cdots\cdots H-O-H$$

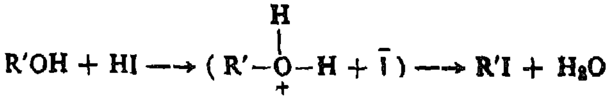
This solubility of ether in water can be reduced to less than half value by saturating the water with common salt (salting out). Ethers are quite similar in nature to hydrocarbons. So ethers are also soluble in hydrocarbons and other non-polar solvents.

17.2-4 REACTIONS

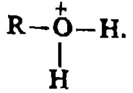
(i) *Cleavage*

Ethers are much less reactive than compounds containing other functional groups. This lack of activity towards most of the reagents makes them useful solvents and media for various reactions They do not react with active metals like sodium or with strong bases like NaOH. Ethers are neither influenced by reducing nor by oxidizing agents unless drastic conditions are used. However, ethers undergo cleavage with concentrated acids under high temperatures. The alkyl group is separated from the alkoxy group


$$R-O-R' + HI \xrightarrow{295\text{-}305K} \left[R-\overset{\overset{H}{|}}{\underset{+}{O}}-R' + \bar{I} \right] \longrightarrow R'OH + RI$$


$$R'OH + HI \longrightarrow (R'-\overset{\overset{H}{|}}{\underset{+}{O}}-H + \bar{I}) \longrightarrow R'I + H_2O$$

This cleavage is normally carried out with hydrogen iodide though hydrogen bromide, HBr is also effective First the ether molecule gets protonated and then reacts with I^- ion to form molecules of alcohol and alkyl iodide. The alcohol thus produced further reacts with H^+ to form



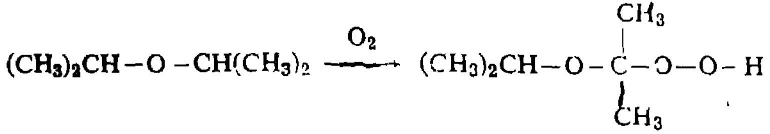
$$R-\underset{\underset{H}{|}}{\overset{+}{O}}-H.$$

This reacts with I^- ions forming the other alkyl halide molecule

The cleavage reaction of mixed ethers in which one group is aliphatic, and the other aromatic, produces phenol and a molecule of alkyl iodide is formed Phenol does not react further as it resists protonation.

(ii) *Peroxide formation*

Ethers on standing in contact with air are slowly converted into peroxides These peroxides are present in old bottles of ethers in low concentrations They are thermally unstable and violent explosions are sometimes caused during distillation of old samples of ethers.



$$(CH_3)_2CH-O-CH(CH_3)_2 \xrightarrow{O_2} (CH_3)_2CH-O-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-O-O-H$$

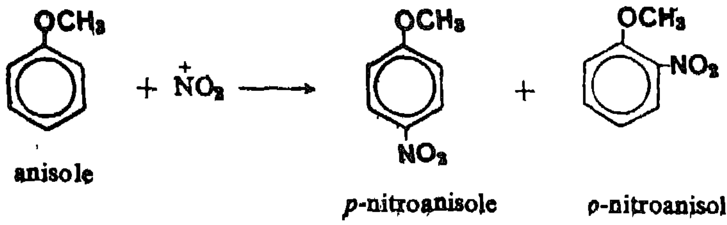
The presence of peroxide in an ether may be detected by shaking it with a freshly prepared aqueous solution of ferrous ammonium sulphate and then adding potassium thiocyanate. The peroxide present oxidizes the ferrous salt to the ferric state, which then reacts with the thiocyanate ion to give the red colour of ferric thiocyanate

$$\text{Peroxides} + Fe^{2+} \longrightarrow Fe^{3+} \xrightarrow{SCN^-} Fe(SCN)_3 \text{ (red)}$$

Peroxides can be removed from ethers by washing them with a solution of a ferrous salt or by distilling them with concentrated sulphuric acid.

(iii) ***Ring substitution in aromatic ethers***

When the alkoxy group, —OR is attached to a benzene ring, it directs new entrant groups to the *ortho* and *para* positions.



17.2.5 USES OF ETHERS

Diethyl ether is used in surgery as a general anaesthetic. It is easy to administer and bring about excellent relaxation of muscles. It is also used as an industrial solvent for oils, fats, gums and resins and as an extracting solvent.

17.3 ALDEHYDES AND KETONES

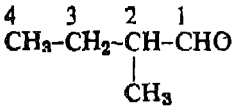
The aldehydes and ketones contain the carbonyl group, $>C=O$ in their structures The general formulae for aldehydes and ketones are $R-\overset{\overset{O}{\|}}{C}-H$ and $R-\overset{\overset{O}{\|}}{C}-R'$ respectively Here R and R′ could be aliphatic or aromatic and they could be the same or different groups.

17.3.1 NOMENCLATURE AND STRUCTURAL FEATURES

The trivial and IUPAC names of the first few members of the homologous series of aldehydes are given below The trivial names of aldehydes follow from the names of acids obtained by their oxidation.

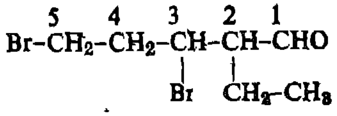
Molecular formula	*Trivial name*	*IUPAC name*
$HCHO$	Formaldehyde	Methanal
CH_3CHO	Acetaldehyde	Ethanal
CH_3CH_2CHO	Propionaldehyde	Propanal
$CH_3CH_2CH_2CHO$	n-butyraldehyde	Butanal

In IUPAC nomenclature of an aldehyde the class suffix is *'al'*. The carbon of the carbonyl group is regarded as the first in the chain of carbon atoms. The longest chain including the –CHO group is selected as the parent hydrocarbon and the aldehyde is named by replacing the 'e' of the corresponding alkane by 'al'.



$\overset{4}{CH_3}-\overset{3}{CH_2}-\underset{CH_3}{\overset{2}{CH}}-\overset{1}{CHO}$

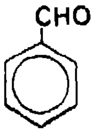
2-methyl butanal

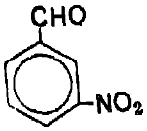


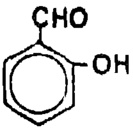
$Br-\overset{5}{CH_2}-\overset{4}{CH_2}-\underset{Br}{\overset{3}{CH}}-\underset{CH_2-CH_3}{\overset{2}{CH}}-\overset{1}{CHO}$

3, 5-dibromo-2-ethylpentanal

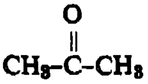
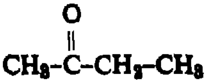
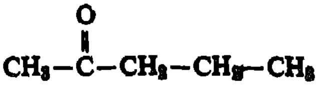
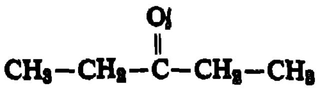
The simplest aromatic aldehyde is benzaldehyde and the names of the other aldehydes may be derived from it


benzaldehyde

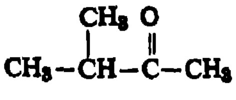

m-nitrobenzaldehyde


o-hydroxybenzaldehyde or (salicylaldehyde)

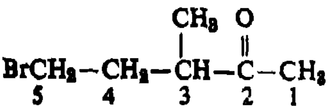
The trivial names of most of aliphatic ketones are given by naming both the alkyl groups attached to the carbon of the carbonyl group ($>C=O$) followed by the word ketone In IUPAC nomenclature, the longest carbon chain including the ketone function is selected. The carbon chain is numbered from end to end so as to give lowest number to the carbon of the carbonyl group. The name of the ketone is derived from that of the corresponding alkane by replacing 'e' of alkane by 'one' and specifying the position of carbon of carbonyl group by a numeral, if necessary. Some examples of ketone nomenclature are as follows :

Formula	*Trivial name*	*IUPAC name*
 $CH_3-\overset{\overset{O}{\|}}{C}-CH_3$	**acetone**	**propanone**
 $CH_3-\overset{\overset{O}{\|}}{C}-CH_2-CH_3$	**ethyl methyl ketone**	**butanone**
 $CH_3-\overset{\overset{O}{\|}}{C}-CH_2-CH_2-CH_3$	**methyl *n*-propyl ketone**	**2-pentanone**
 $CH_3-CH_2-\overset{\overset{O}{\|}}{C}-CH_2-CH_3$	**diethyl ketone**	**3-pentanone**

Similarly the ketones carrying the substituents are named :

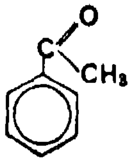

$CH_3-\overset{\overset{CH_3}{|}}{C}H-\overset{\overset{O}{\|}}{C}-CH_3$

3-methyl-2-butanone

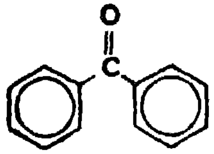

$\underset{5}{BrCH_2}-\underset{4}{CH_2}-\underset{3}{\overset{\overset{CH_3}{|}}{C}H}-\underset{2}{\overset{\overset{O}{\|}}{C}}-\underset{1}{CH_3}$

5-bromo-3-methyl-2-pentanone

Examples of aromatic ketones are:

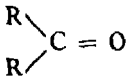


acetophenone

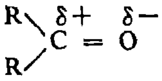


benzophenone

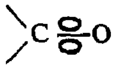
From the general formulae for aldehydes and ketones we see that the only difference between the two is that in aldehydes the carbonyl group ($>C=O$) is attached to one hydrogen and one alkyl or aryl group while in ketones it is attached to two alkyl or aryl groups, or one alkyl and one aryl groups However, in formaldehyde two hydrogen atoms are attached to the $>C=O$ group. The carbonyl group, $>C=O$, is largely responsible for the characteristic reactions of aldehydes and ketones and we may well expect that some of these reactions will be common for aldehydes and ketones



$$\begin{matrix} R \\ R \end{matrix}\!>\!C=O$$



$$\begin{matrix} R \\ R \end{matrix}\!>\!\overset{\delta+}{C}=\overset{\delta-}{O}$$

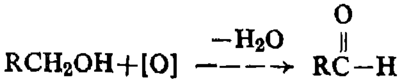


The carbonyl group consists of a carbon and an oxygen atom which are linked by a double bond. It has a formal resemblance to the olefinic carbon-carbon double bond. The sp^2 hybridized carbon is joined to three substituents by three σ bonds utilizing all the three sp^2 hybridized orbitals. All these lie in one plane making an angle of 120° with one another The fourth unhybridised p-orbital of carbon atom overlaps with a p-orbital of oxygen atom to form a bond. This bond, in contrast to the π-bond in alkenes, connects two atoms of different electronegativity and hence the bonding electrons are not equally shared by the linked atoms. The electron cloud lies more towards the oxygen atom. This polarization of electron cloud results in a high dipole-moment (2.3 to 2.8D) for carbonyl compounds.

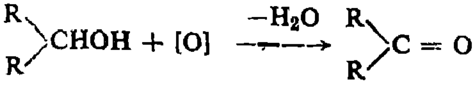
17.3.2 LABORATORY PREPARATION OF ALDEHYDES AND KETONES

(*i*) *From alcohols*: Aldehydes are prepared by the oxidation of primary alcohols under controlled conditions. Oxidation of secondary alcohols yields

ketones. The common oxidizing agents used are potassium dichromate and potassium permanganate.



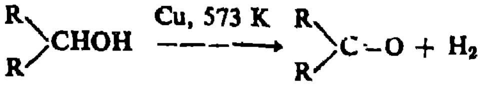
$$RCH_2OH + [O] \xrightarrow{-H_2O} R\overset{O}{\overset{\|}{C}}-H$$



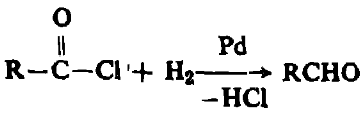
Aldehydes are even more easily oxidized than the alcohols from which they are derived. Oxidation of aldehydes gives corresponding carboxylic acids. In order to control this oxidation, advantage is taken of higher volatility of aldehydes compared to the corresponding alcohols. For example, butanal (b. p. 349K) has boiling point 42° lower than 1-butanol (b.p. 391K). When a mixture of dichromate and sulphuric acid is added drop by drop to alcohol contained in a flask, aldehyde formed is immediately distilled out through the condenser attached to the flask. Since the aldehyde is taken out of the oxidizing mixture by distillation as soon as it is formed its further oxidation to acid is minimized. A fractionating column may be used to hold back vapour of alcohol.

Another way of preparing aldehydes and ketones is through catalytic dehydrogenation of primary and secondary alcohols Alcohol vapour is passed over heated copper gauze Oxidation of aldehydes to acids has no chance in this case.

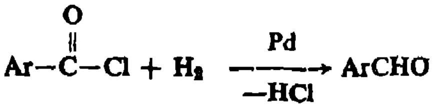
$$RCH_2OH \xrightarrow{Cu,\ 573\ K} RCHO + H_2$$



(ii) *From acid chlorides* : Acid chlorides are reduced to aldehydes with hydrogen in the presence of palladium catalyst spread on barium sulphate. This is known as ***Rosenmund reduction.***



$$R-\overset{O}{\overset{\|}{C}}-Cl + H_2 \xrightarrow[-HCl]{Pd} RCHO$$

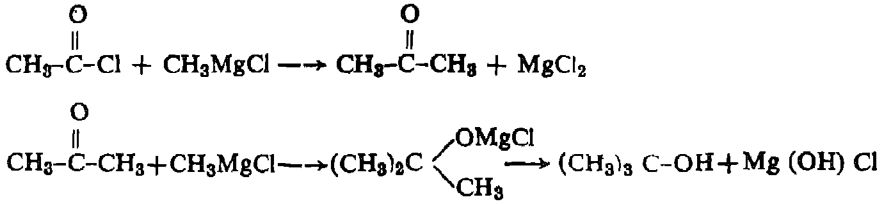


$$Ar-\overset{O}{\overset{\|}{C}}-Cl + H_2 \xrightarrow[-HCl]{Pd} ArCHO$$

Ketones are prepared by reacting acid chlorides with dialkyl cadmium.

$$2RCOCl + CdR'_2 \dashrightarrow 2RCOR' + CdCl_2$$

Direct reaction of an acid chloride with a Grignard reagent gives a ketone which further reacts with Grignard reagent to give a tertiary alcohol. This difficulty is avoided by using a dialkyl cadmium.



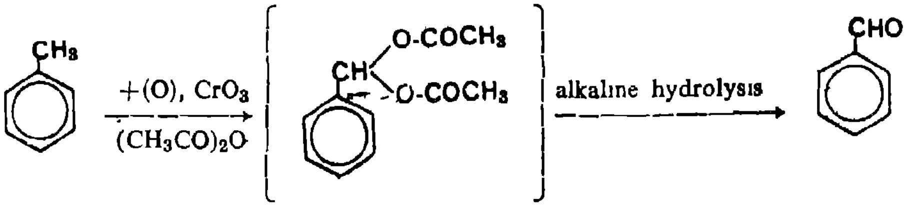
$$CH_3-\overset{O}{\overset{\|}{C}}-Cl + CH_3MgCl \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + MgCl_2$$

$$CH_3-\overset{O}{\overset{\|}{C}}-CH_3+CH_3MgCl \longrightarrow (CH_3)_2C\begin{matrix}\diagup OMgCl\\ \diagdown CH_3\end{matrix} \longrightarrow (CH_3)_3\,C-OH+Mg\,(OH)\,Cl$$

Aromatic aldehydes and ketones are prepared by methods which are generally not applicable in the aliphatic series. Some of these methods are discussed below ;

(i) Oxidation of side-chain alkyl groups

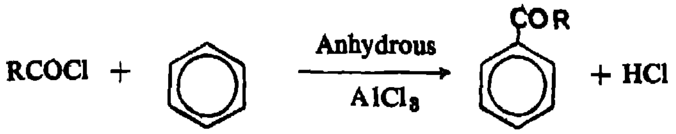
Aromatic aldehydes are prepared by oxidation of a side chain in an aromatic compound using chromium trioxide. Further oxidation of the aldehyde to an acid is avoided by trapping the aldehyde in the form of a non-oxidizable derivative with acetic anhydride.

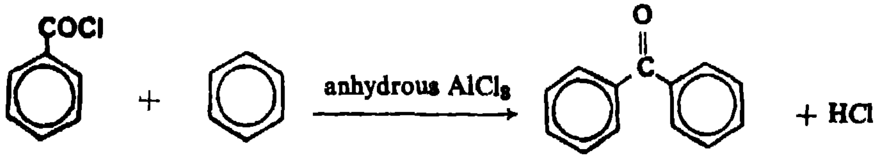


*(ii) Aromatic ketones through Friedel-Crafts acylation**

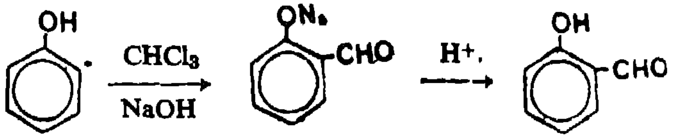
Aromatic ketones are prepared by treating the aromatic hydrocarbons with acid chlorides in the presence of anhydrous aluminium chloride. This reaction is analogous to Friedel-Crafts alkylation reaction (Part I).

Attachment of $R-\overset{O}{\overset{\|}{C}}-$(acyl group) to a compound is called *acylation* and that of $CH_3-\overset{O}{\overset{\|}{C}}-$ (acetyl group) is known as *acetylation*.





Reimer-Tieman Reaction : We have already seen (Sec. 17.1-4) that phenolic aldehydes can be prepared by treating phenol with chloroform in basic medium at 343 K.



Industrial preparations

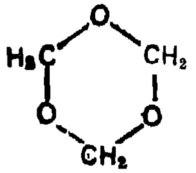
Formaldehyde, HCHO : Formaldehyde is widely used in various industries. It is manufactured by the oxidation of methanol in the presence of a catalyst using oxygen from air.

$$CH_3OH + O_2 \xrightarrow{Cu,\ 825\text{-}875\ K} HCHO + H_2O$$

Formaldehyde is a gas at room temperature, b. p. 252 K. Its 40 per cent solution in water is sold under the name *formalin*. It is also available as a solid polymer, *paraformaldehyde* $(CH_2O)_n$ and *trioxane*, $(CH_2O)_3$.

$\sim CH_2O\text{-}CH_2O\text{-}CH_2O \sim$

paraformaldehyde



trioxane

Whenever formaldehyde is required, it can be obtained by heating paraformaldehyde or trioxane.

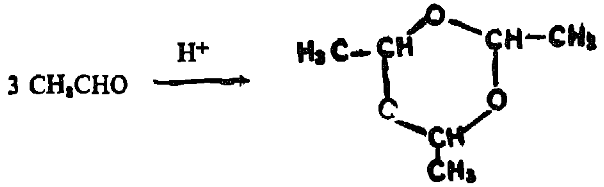
Acetaldehyde, CH_3CHO : Acetaldehyde is normally used for the manufacture of acetic acid. The trimer of acetaldehyde which is used as a hypnotic in medicines, is called *paraldehyde*. When acetylene is hydrated with dilute sulphuric acid in the presence of $HgSO_4$, it gives acetaldehyde. This constitutes the industrial method for the manufacture of acetaldehyde.

$$CH \equiv CH + H_2O \xrightarrow[1\%\ HgSO_4]{40\%\ H_2SO_4} CH_3CHO$$

Acetaldehyde is also manufactured by the dehydrogenation of ethyl alcohol in the presence of Cu heated to 573K.

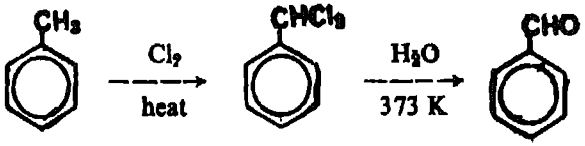
$$CH_3CH_2OH \xrightarrow{Cu,\ 573K} CH_3CHO + H_2$$

Acetaldehyde is avilable as its trimer, paraldehyde, $(CH_3CHO)_3$ which can be prepared by adding a drop of conc. H_2SO_4 to acetaldehyde or by keeping acetaldehyde for a long time.



Acetaldehyde can be reformed by warming paraldehyde with dil. H_2SO_4

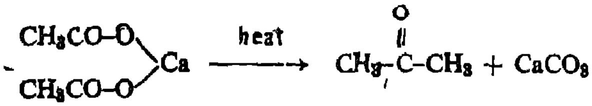
Benzaldehyde, C_6H_5CHO : It is an aromatic aldehyde. It is used in perfumery and in the manufacture of dyes. It is commercially prepared by side chain chlorination of toluene followed by hydrolysis of the resulting compound.



Acetone, CH_3COCH_3: It is a common solvent for use in laboratories and in various industries. It is manufactured by dehydrogenation of iso-propyl alcohol using heated copper.

$$CH_3CHOHCH_3 \xrightarrow{Cu,\ 573\ K} CH_3COCH_3 + H_2$$

Some acetone is also obtained as a by-product during fermentation of starch in the preparation of ethyl alcohol. It is one of the products in wood distillation. Some acetone is also prepared by the dry distillation of calcium acetate.



$$(CH_3CO-O)_2Ca \xrightarrow{heat} CH_3-\overset{\overset{O}{\|}}{C}-CH_3 + CaCO_3$$

17.3-3 PHYSICAL PROPERTIES

Aldehydes and ketones are polar compounds because of the presence of carbonyl group. As a result they have intermolecular attractions which make them somewhat higher boiling than the hydrocarbons of comparable molecular masses. These intermolecular attractions are weaker than those due to hydrogen bonds in alcohols. Consequently, aldehydes and ketones are lower boiling liquids than alcohols of comparable molecular masses.

Compounds	*b. p. (K)*
n-butyraldehyde	349
n-butane	309
n-butyl alcohol	391

The lower aldehydes and ketones upto four carbons per molecule are soluble in water because of some hydrogen bonding between $>C=O$ groups and water molecules and smaller size of the alkyl groups attached to $>C=O$ group. Solubility decreases as the hydrocarbon part in the molecule increases. Aldehydes and ketones are quite soluble in organic solvents.

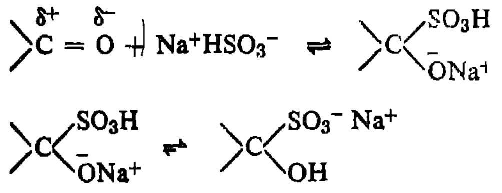
17.3-4 CHEMICAL PROPERTIES OF ALDEHYDES AND KETONES

These are centred at the carbonyl group ($>C=O$). Due to the polarization in $>C=O$, the carbon atom acquires a partial positive charge and the oxygen atom acquires a partial negative charge. The polar nature of carbonyl group leads to a number of addition reactions with other polar compounds.

The aldehydes in general undergo addition reactions more readily than the ketones.

ADDITION REACTIONS

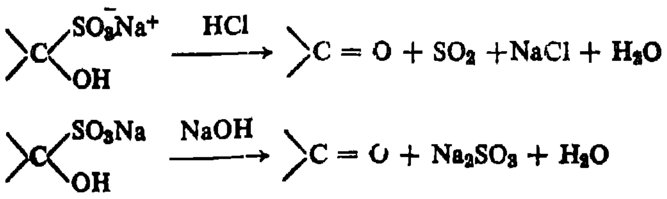
(i) *Addition of sodium bisulphite*: Most of aldehydes and methyl ketones add sodium bisulphite at the $>C = O$ group to form bisulphite addition product.



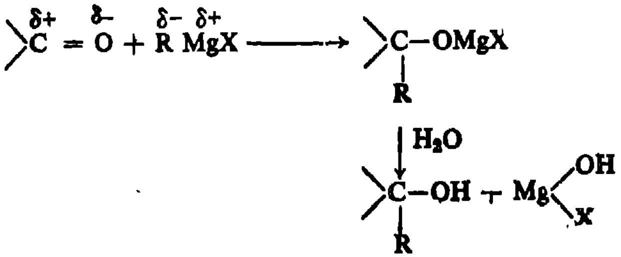
bisulphite addition product

This addition reaction is carried out by shaking the aldehyde or ketone with a saturated aqueous solution of sodium bisulphite. The addition product is often a crystalline solid. The reaction is used in the purification of aldehydes and ketones and their separation from substances that do not react with sodium bisulphite.

The crystalline solid after separation from the rest of material regenerates the original carbonyl compound on treatment with an acid or an alkali.

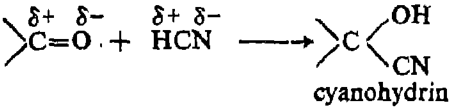


(ii) *Addition of Grignard reagents*: We have studied in the last Unit that Grignard reagents are added to aldehydes and ketones to give product from which secondary and tertiary alcohols respectively may be obtained.

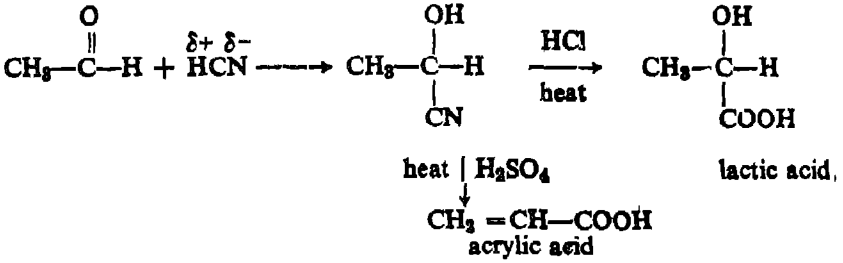


The alkyl group in Grignard reagent is transferred to the carbon of the carbonyl group. The resulting addition compound is very easily hydrolyzed to give an alcohol.

(iii) *Addition of hydrogen cyanide*: Hydrogen cyanide when added to aldehydes and ketones forms cyanohydrin



This reaction is normally carried out in the presence of a base acting as catalyst. In the absence of a base the reaction proceeds extremely slowly. In actual practice hydrogen cyanide is generated *in situ* by the addition of a strong acid to a mixture of sodium cyanide and the carbonyl compound. The amount of acid added is insufficient to react with the whole of sodium cyanide. As a result the solution remains sufficiently alkaline to catalyse the addition. The principal use of cyanohydrins is that they can be converted into 2-hydroxy acids and unsaturated acids.



$$CH_3-\overset{\overset{O}{\|}}{C}-H + \overset{\delta+\ \delta-}{HCN} \longrightarrow CH_3-\underset{\underset{CN}{|}}{\overset{\overset{OH}{|}}{C}}-H \xrightarrow[\text{heat}]{HCl} CH_3-\underset{\underset{COOH}{|}}{\overset{\overset{OH}{|}}{C}}-H$$

lactic acid,

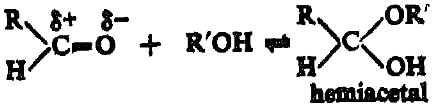
$$\big\downarrow \text{heat} \mid H_2SO_4$$

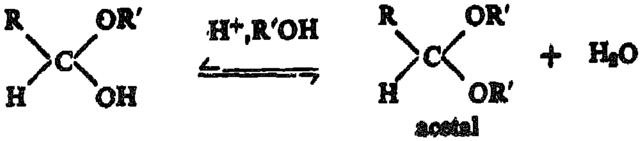
$$CH_2=CH-COOH$$

acrylic acid

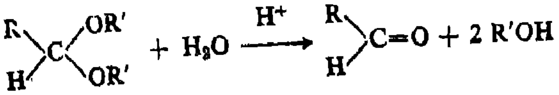
(iv) *Addition of alcohols : Acetal formation*: Aldehydes react with alcohols in the presence of dry hydrogen chloride to form acetals. This reaction is normally carried out by passing dry hydrogen chloride in a mixture of an aldehyde and excess of alcohol.

A hemiacetal is first formed by the addition of an alcohol molecule to the carbonyl group. Hemiacetal is both an ether and an alcohol and in most of the cases, too unstable to be isolated. Hemiacetal reacts with another molecule of alcohol to form a stable *acetal*.



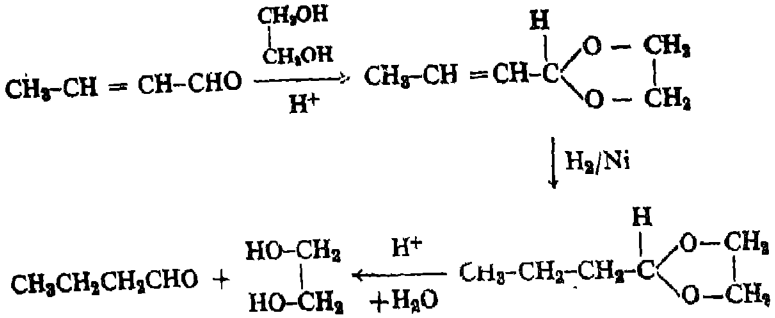


Acetal is the general name of compounds obtained by the reaction between aldehydes and alcohols. Acetals are similar to ethers in behaviour. They are quite unreactive in most of the reactions and can be cleaved readily by acids (but not alkalies) to regenerate the aldehydes.

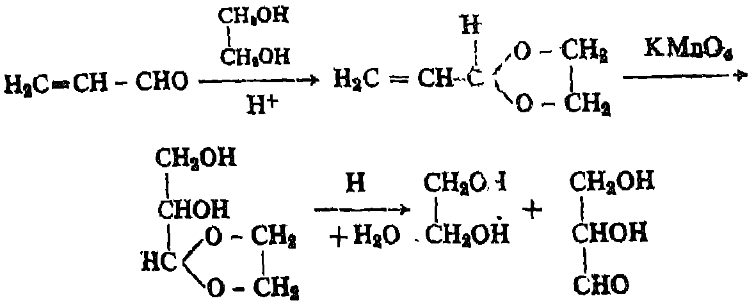


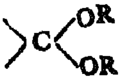
If instead of using two molecules of a monohydric alcohol one molecule of a dihydric alcohol like ethylene glycol ($CH_2OH.CH_2OH$) is used, a cyclic acetal is formed. Acetal formation can be used to protect a carbonyl compound in a reaction as shown below :

(a)



(b)



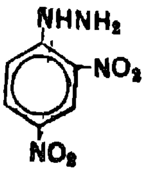
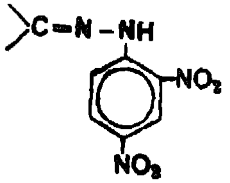
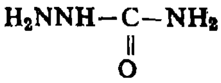
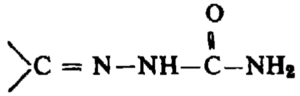
Ketones do not react with alcohols in presence of HCl gas like aldehydes. However, the compounds in which >C=O group of a ketone is converted to  group are called *ketals*. . They are prepared indirectly.

(v) *Addition of ammonia derivatives :* A number of organic compounds containing $-NH_2$ group, condense with >C=O group of aldehydes and ketones to give

$>C=N-$ type of groups with elimination of water These important derivatives of aldehydes and ketones can be used to characterize and identify them.

$$YNH_2 + O{=}C\langle \xrightarrow{H^+} \rangle C{=}NY + H_2O$$

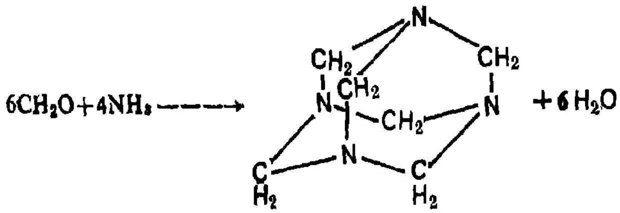
A few typical examples are given below:

Reagent used		Product obtained	
Ammonia Derivative	Name	Structure	Name
H_2NOH	hydroxylamine	$>C=N-OH$	oxime
$H_2NNHC_6H_5$	phenyl hydrazine	$>C=N-NHC_6H_5$	phenyl hydrazone
	2, 4-dinitrophenyl hydrazine		2, 4-dinitrophenyl hydrazone
 $H_2NNH-\underset{\underset{O}{\Vert}}{C}-NH_2$	semicarbazide	 $>C=N-NH-\overset{\overset{O}{\Vert}}{C}-NH_2$	semicarbazone

Like ammonia these derivatives are basic in nature. They are easily oxidized by air. Therefore, they are stored as their salts e.g., hydroxyl amine hydrochloride, $H_3\overset{+}{N}OHCl^-$; phenyl hydrazine hydrochloride, $C_6H_5NH\overset{+}{N}H_3\bar{C}l$; semicarbazide hydrochloride, $H_3\overset{+}{N}-NH-\overset{\overset{O}{\Vert}}{C}-NH_2\bar{C}l$. Whenever needed for a reaction, the base is liberated in the presence of the carbonyl compound by a mild base (usually sodium acetate).

$$ClH_3\overset{+}{N}NHCONH_2 + CH_3COONa \longrightarrow H_2NNHCONH_2 + CH_3COOH + NaCl$$

These addition reactions are catalyzed by the presence of a small amount of some acid because they proceed through a step involving protonation of $>C=O$ group. But if the acid is taken in excess, it would react with the ammonia derivative to form a salt as $R-\overset{+}{N}H_3X$ which does not react An optimum value of pH is needed for the reaction depending on the nature of the base used. Ammonia and formaldehyde react to give hexamethylene tetramine which is a urinary antiseptic.



hexamethylene tetramine

OTHER REACTIONS

Oxidation : Aldehydes are a group of easily oxidizable compounds. In aldehydes there is a hydrogen attached to the carbonyl group which can be converted to OH group in oxidation reactions without needing a breaking up of some other bond and this makes aldehydes easily oxidizable. This property makes distinction of aldehydes from ketones easy. Ketones do not have any hydrogen atom attached to the $>C=O$ group and hence they can not be oxidized without the cleavage of some carbon-carbon bond. So ketones are resistant to usual oxidizing agents. The aldehydes can be oxidized even by mild oxidizing agents like silver ions and cupric ions under basic conditions. These metal ions are reduced to a mirror of metallic silver and to a red precipitate of cuprous oxide respcetively.

$$RCHO + 2Ag^+ + 3\overset{-}{OH} \longrightarrow RCO\overset{-}{O} + \underset{\substack{\text{silver}\\\text{mirror}}}{2Ag} + 2H_2O$$

$$RCHO + 2Cu^{2+} + 5\overset{-}{OH} \longrightarrow RCO\overset{-}{O} + \underset{\text{red ppt}}{Cu_2O} + 3H_2O$$

Silver ions are provided by Tollens reagent. Tollens reagent is made by the addition of ammonium hydroxide to silver nitrate until the brown precipitate of silver oxide first formed is just redissolved. Silver ion is present as a complex with ammonia,

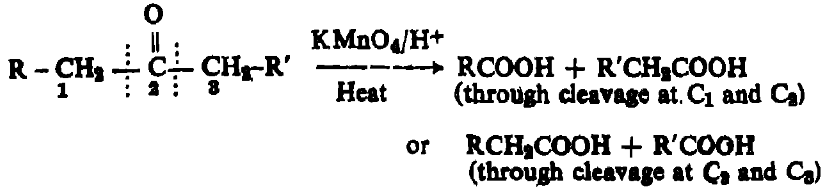
$Ag(NH_3)_2^+$, which prevents the precipitation of silver oxide in the basic solution. Reduction of Tollens reagent to a silver mirror is also known as *silver mirror test.*

Cupric ions are provided by Benedict's and Fehling's solutions. In these reagents hydroxy acids are used to form soluble complexes with cupric ions in basic solutions (citric acid is used in Benedict solution and tartaric acid in Fehling solution). The complexing of cupric ions prevents the precipitation of cupric hydroxide on making the solution alkaline.

Tollen's reagent oxidizes both aliphatic and aromatic aldehydes but Fehling and Benedict solutions oxidize only aliphatic aldehydes. These oxidizing agents do not attack the unsaturation centres in a molecule and thus they are quite useful in oxidizing the unsaturated aldehydes to the corresponding acids.

$$R-CH=CH-CHO \xrightarrow{\text{Tollens reagent}} R-CH=CH-COOH$$

Oxidation of ketones requires cleavage of carbon-carbon bond and takes place only under vigorous conditions. On oxidation ketones give mixtures of acids.

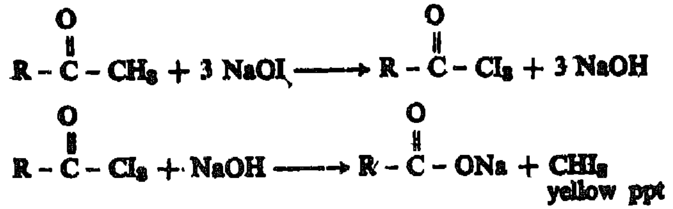


$$\underset{1}{R-CH_2}\,\vdots\,\underset{2}{\overset{O}{\overset{\|}{C}}}\,\vdots\,\underset{3}{CH_2-R'} \xrightarrow[\text{Heat}]{KMnO_4/H^+} \underset{(\text{through cleavage at } C_1 \text{ and } C_2)}{RCOOH + R'CH_2COOH}$$

$$\text{or} \quad \underset{(\text{through cleavage at } C_2 \text{ and } C_3)}{RCH_2COOH + R'COOH}$$

However, all methyl ketones and acetaldehyde can be easily oxidized with a hypohalite solution to yield a haloform. This reaction is called *haloform reaction.* When hypoiodite is used for oxidation, a yellow precipitate of iodoform is obtained.

This is used as a test for $CH_3-\overset{O}{\overset{\|}{C}}-$ *group.



$$R-\overset{O}{\overset{\|}{C}}-CH_3 + 3\,NaOI \longrightarrow R-\overset{O}{\overset{\|}{C}}-CI_3 + 3\,NaOH$$

$$R-\overset{O}{\overset{\|}{C}}-CI_3 + NaOH \longrightarrow R-\overset{O}{\overset{\|}{C}}-ONa + \underset{\text{yellow ppt}}{CHI_3}$$

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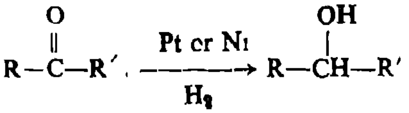
*Compounds like C_2H_5OH and $RCHOHCH_3$ also give iodoform test because NaOI first oxidises them to $CH_3-\overset{O}{\overset{\|}{C}}-H$ and $R-\overset{O}{\overset{\|}{C}}-CH_3$ respectively.

(*ii*) ***Reduction*** : Aldehydes and ketones on reduction give primary and secondary alcohols respectively. Reduction can be carried through catalytic hydrogenation or by chemical reagents like lithium aluminium hydride or sodium borohydride.



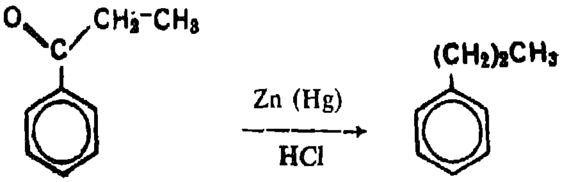
$$R-\overset{\overset{O}{\|}}{C}-R' \xrightarrow[H_2]{Pt\ or\ Ni} R-\overset{\overset{OH}{|}}{C}H-R'$$

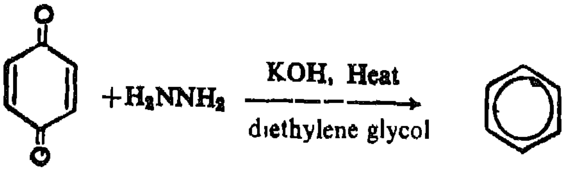
$$RCHO \xrightarrow[\text{or } NaBH_4]{LiAlH_4} RCH_2OH$$

If a double bond is also present in the compound, catalytic hydrogenation will reduce this also, but sodium borohydride reduces only the carbonyl group

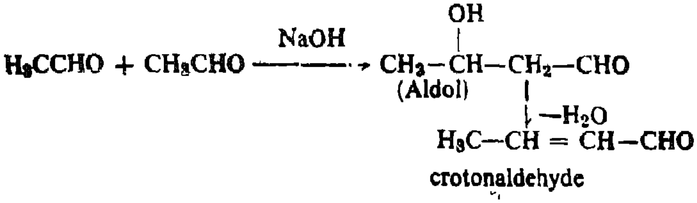
$$H_3C-CH=CH-CHO \begin{cases} \xrightarrow{H_2/Ni} CH_3CH_2CH_2CH_2OH \\ \xrightarrow[NaBH_4]{} H_3C-CH=CH-CH_2OH \end{cases}$$

Aldehydes and ketones can be reduced to corresponding hydrocarbons either by Clemmensen reduction or by Wolff-Kishner reduction. Clemmensen reduction involves refluxing the carbonyl compound with zinc amalgam and hydrochloric acid. Wolff-Kishner reduction requires heating the carbonyl compound in a high boiling polar solvent like diethylene glycol with hydrazine and potassium hydroxide and driving the reaction to completion by distilling out the water formed.





(*iii*) *Aldol Condensation* : Aldehydes and ketones which have atleast one α-hydrogen* condense in dilute alkali to give a condensation product. This reaction is called *Aldol condensation*



$$H_3CCHO + CH_3CHO \xrightarrow{NaOH} \underset{\text{(Aldol)}}{CH_3-\overset{\overset{OH}{|}}{C}H-CH_2-CHO} \xrightarrow{-H_2O} \underset{\text{crotonaldehyde}}{H_3C-CH = CH-CHO}$$

Aldehydes with α-hydrogens form resins on being heated with concentrated alkali.

(*iv*) *Cannizzaro reaction* : Aldehydes like formaldehyde or benzaldehyde which do not have α-hydrogen undergo self condensation in the presence of a concentrated alkali to give a mixture of an alcohol and salt of a carboxylic acid.

$$2\,HCHO \xrightarrow{NaOH} CH_3OH + HCOONa$$

$$2C_6H_5CHO \xrightarrow{NaOH} C_6H_5CH_2OH + C_6H_5COONa$$

One molecule of aldehyde is oxidized to acid and the other is reduced to alcohol.

17.3-5 TESTS FOR ALDEHYDES AND KETONES

Aldehydes and ketones are characterized through the formation of 2,4-dinitrophenyl hydrazone derivatives. Aldehydes are distinguished from ketones through their ease of oxidation. Aldehydes give positive tests with Tollens Schiff, Fehling or Benedict reagents whereas ketones do not. Generally aldehydes and ketones are identified through the melting points of their derivatives like oximes, semicarbazones and 2,4-dinitrophenyl hydrazones. Methyl ketones are identified through *Iodoform test*.

17.4 CARBOXYLIC ACIDS

The functional group which characterizes carboxylic acids is $-\overset{\overset{O}{\|}}{C}-OH$ (carboxyl group). It may be attached to an alkyl (—R) or an aryl (—Ar), group Some of the higher members of aliphatic series of acids are obtained by hydrolysis of fats; therefore, the group of aliphatic carboxylic acids is also known as fatty acid group.

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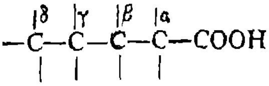
*The carbon next to the carbon of—CHO groups in aldehyde is called α-carbon and hydrogen attached to it is known α- hydrogen, $-\underset{|}{\overset{|\gamma}{C}}-\underset{|}{\overset{|\beta}{C}}-\overset{|\alpha}{C}-CHO$

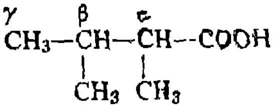
17.4.1 NOMENCLATURE

The trivial and the IUPAC names of ~~the~~ first few members are given below :

Molecular formulae	Trivial names	IUPAC names
$HCOOH$	formic acid	methanoic acid
CH_3COOH	acetic acid	ethanoic acid
CH_3CH_2COOH	propionic acid	propanoic acid
$CH_3CH_2CH_2COOH$	butyric acid	butanoic acid

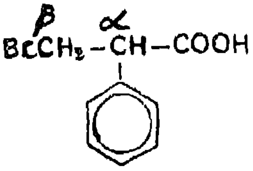
The trivial names in general have been derived from the names of common sources for acids*. In this nomenclature the carbon atoms in the chain are designated by Greek letters α, β, γ, δ, etc. starting from the carbon adjacent to carboxylic group :





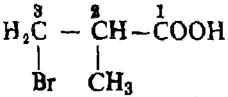
$$CH_3-\underset{CH_3}{\underset{|}{CH}}-\underset{CH_3}{\underset{|}{CH}}-COOH$$

α, β—dimethyl butyric acid



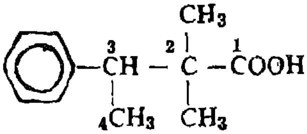
β-bromo-α-phenyl propionic acid

In the IUPAC nomenclature of aliphatic acids, the ending 'e' of the alkane having an equal number of carbon atoms in the molecule is replaced by 'oic acid'. The longest carbon chain carrying the carboxyl group is selected and numbering is done with carboxyl carbon as position one.



$$\underset{Br}{\underset{|}{\overset{3}{H_2C}}}-\underset{CH_3}{\underset{|}{\overset{2}{CH}}}-\overset{1}{C}OOH$$

3-bromo -2-methyl propanoic acid



2, 2-dimethyl 3-phenyl butanoic acid

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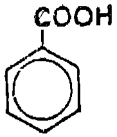
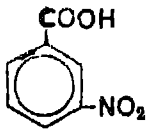
[*] Formic acid was prepared for the first time from red ants (Latin : *formicus* means ant). Acetic acid is derived from the Latin word *acetum* which means vinegar (a source of acetic acid). Butyric acid smells like rancid butter (Latin : butyrum means butter).

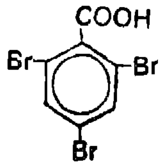
Names of aromatic acids are normally derived from the parent acid, benzoic acid, C_6H_5COOH.



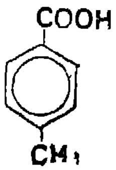
benzoic acid



(*m*-nitrobenzoic acid)
or 3-nitrobenzoic acid



2, 4, 6-tribromo-
benzoic acid



p-toluic acid
(from toluene)

17.4-2 LABORATORY PREPARATION

In the laboratory carboxylic acids can be prepared by the following general methods :

1. Oxidations

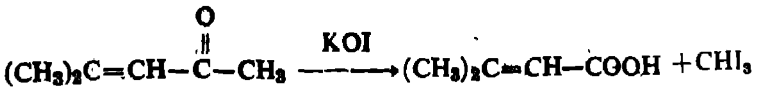
(*a*) *From primary alcohols* . We have already learnt that primary alcohols on oxidation yield aldehydes which on further oxidation yield carboxylic acids The oxidizing agents normally used are potassium permanganate or dichromate in sulphuric acid.

$$RCH_2OH \xrightarrow[\text{or } K_2Cr_2O_7/H_2SO_4]{KMnO_4} RCOOH$$

(b) *From aldehydes and ketones* : Aldehydes can be easily oxidized to carboxylic acids even with mild oxidizing agents like Tollens reagent.

$$RCHO+2Ag(NH_3)_2^{+}+3OH^{-} \longrightarrow 2Ag+RCOO^{-}+4NH_3+2H_2O$$

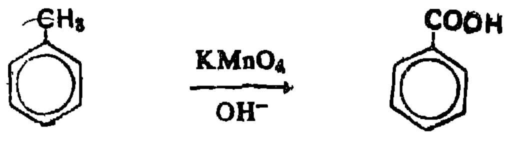
Methyl ketones are smoothly oxidized with hypohalite solutions



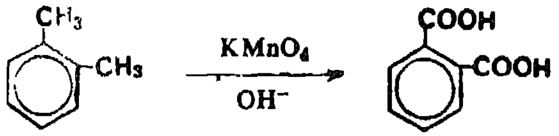
$$(CH_3)_2C{=}CH-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow{KOI} (CH_3)_2C{=}CH-COOH+CHI_3$$

The oxidation of other ketones yields acids under very strong oxidizing conditions and, usually mixed products are obtained. Therefore, the preferred method of preparation of carboxylic acids is oxidation of primary alcohols or aldehydes in which the carbon skeleton remains the same.

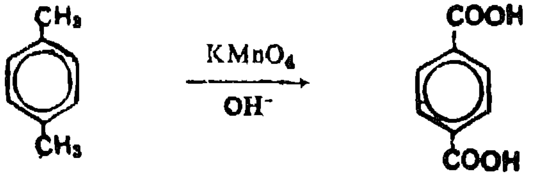
(c) *Oxidation of alkyl benzenes* : An alkyl group attached to an aromatic ring is oxidized to a carboxylic group irrespective of the size of alkyl group. Alkaline potassium permanganate is generally used as an oxidizing agent for this purpose. Potassium dichromate or dilute nitric acid can also be used.



toluene benzoic acid



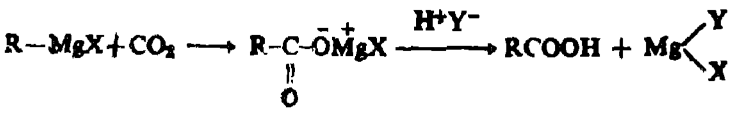
o-xylene phthalic acid



p-xylene terephthalic acid

2. From Grignard Reagents

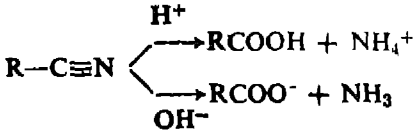
An ethereal solution of a Grignard reagent reacts with carbon dioxide. This reaction is normally carried out either by bubbling carbon dioxide in an ethereal solution of a Grignard reagent or by adding the solution of Grignard reagent to powdered solid carbon dioxide suspended in ether. The addition product is decomposed with a mineral acid to liberate the free acid.



$$R-MgX + CO_2 \longrightarrow R-\underset{\underset{O}{\|}}{C}-\overset{-}{O}\overset{+}{M}gX \xrightarrow{H^+Y^-} RCOOH + Mg\begin{matrix} Y \\ X \end{matrix}$$

3. From Cyanides

Alkyl cyanides are hydrolyzed to carboxylic acids by boiling either with an alkali or an acid

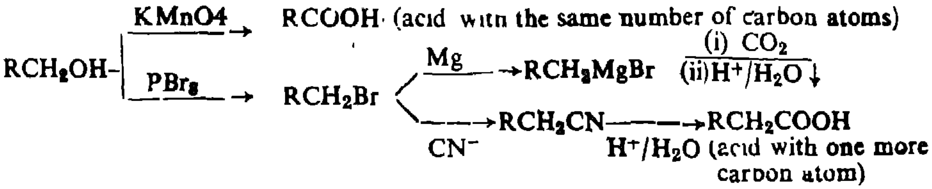


$$R{-}C{\equiv}N \begin{cases} \xrightarrow{H^+} RCOOH + NH_4^+ \\ \xrightarrow[OH^-]{} RCOO^- + NH_3 \end{cases}$$

Alkyl cyanides are easily prepared from the corresponding alkyl halides by treatment with potassium cyanide solution.

$$RX + KCN \longrightarrow RCN + KX$$

Since alkyl halides can be prepared from alcohols, we have methods for converting a primary alcohol either to an acid containing the same number of carbon atoms or to an acid containing one carbon atom more.



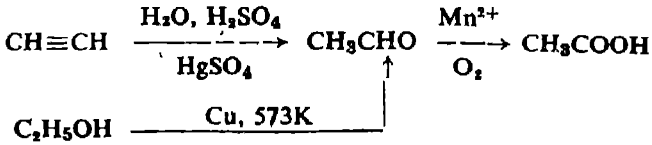
$$\begin{array}{l} RCH_2OH \xrightarrow{KMnO4} RCOOH \text{ (acid with the same number of carbon atoms)} \\ RCH_2OH \xrightarrow{PBr_3} RCH_2Br \begin{cases} \xrightarrow{Mg} RCH_2MgBr \xrightarrow[(ii) H^+/H_2O]{(i)\ CO_2} \\ \xrightarrow[CN^-]{} RCH_2CN \xrightarrow[H^+/H_2O]{} RCH_2COOH \text{ (acid with one more carbon atom)} \end{cases} \end{array}$$

17.4-3 INDUSTRIAL PREPARATION

Formic acid which is used in various industries is prepared on a large scale by reacting carbon monoxide with aqueous sodium hydroxide under a pressure of 1 atm at 473K

$$CO + NaOH\,(aq) \xrightarrow[1\ atm]{473K} HCOONa \xrightarrow{H^+} HCOOH$$

Acetic acid is another very important carboxylic acid. It is manufactured (i) by the hydration of acetylene to acetaldehyde which is further oxidized to acetic acid with air in the presence of manganous acetate, (ii) by the dehydrogenation of ethyl alcohol with copper at 523-573K to acetaldehyde followed by further oxidation.

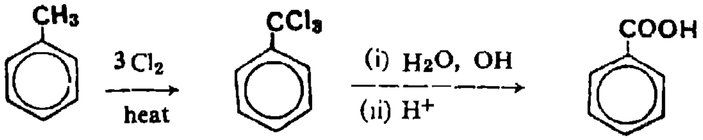


$$\begin{tikzcd}
CH\equiv CH \arrow[r, "H_2O,\ H_2SO_4", "HgSO_4"'] & CH_3CHO \arrow[r, "Mn^{2+}", "O_2"'] & CH_3COOH \\
C_2H_5OH \arrow[ru, "Cu,\ 573K"'] & &
\end{tikzcd}$$

A dilute solution of acetic acid is known as *vinegar*. It is manufactured by fermentation of ethyl alcohol with special bacteria (*acetobacter*) in the presence of air. Vinegar has been prepared by this method since times immemorial.

$$CH_3CH_2OH + O_2 \xrightarrow{\text{acetobacter}} CH_3COOH + H_2O$$

Higher aliphatic carboxylic acids are obtained from vegetable fats. These carboxylic acids have even numbers of carbon atoms (ranging from six to eighteen) An important aromatic carboxylic acid is benzoic acid. It is manufactured by oxidation of toluene which is readily available from coal tar and from petroleum. Benzoic acid can also be prepared by chlorination of toluene followed by hydrolysis.



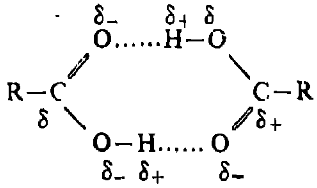
17 4-4 PHYSICAL PROPERTIES

As would be evident from their structures, the carboxylic acids are polar compounds which can form hydrogen bonds. This fact is reflected in their physical properties

Amongst aliphatic acids, the lower homologues (upto C_4) are miscible with water, the higher ones are practically insoluble due to the increased influence of hydrocarbon part The effect of the carboxylic group which makes an acid water soluble due to hydrogen bonding with water molecules is thus significant in the first few members only, and decreases gradually with the increase in the size of the alkyl group causing the solubility in water to diminish.

Benzoic acid, the simplest aromatic carboxylic acid is nearly insoluble in cold water because the hydrocarbon part outweighs the influence of the polar part. Carboxylic acids are also soluble in less polar solvents like ether, alcohol, benzene, etc.

The first three members of the aliphatic series (C_1 to C_3) are colourless, pungent smelling liquids, the next three (C_4–C_6) have distinctly unpleasant odours. Acids with seven or more carbon atoms have no distinct smell because of low volatility. Carboxylic acids are higher boiling than alcohols of comparable molecular masses (*n*-propyl alcohol . b.p. 370K, acetic acid ,b.p. 391K). This is due to intermolecular hydrogen bonding leading to dimer formation in which two acid molecules are held together by two hydrogen bonds.



hydrogen bonding

The existence of such dimers is clearly indicated in solutions of acetic acid in solvents like benzene when the observed colligative properties lead to a molecular mass of 120 instead of 60.

In straight chain aliphatic carboxylic acids, one with even number of carbon atoms per molecule has a higher melting point than the one with odd numbers of carbon atoms immediately below and above it. The curve plotted between the number of carbon atoms per molecule and the melting point is a zig-zag one and resembles a saw-tooth (compare alkanes, Part-I). It has been shown by X-ray diffraction that even-number acids have carboxyl and terminal methyl groups on the opposite sides of the zig-zag carbon chain and fit better in the crystal lattice, thereby increasing intermolecular forces resulting in higher melting points. The odd number acids have carboxyl and terminal methyl groups on the same side. Benzoic acid and most other aromatic acids are solids because of their polar nature and higher molecular masses.

17.4-5 CHEMICAL REACTIONS

1. *Acidity*: The carboxylic acids are the most acidic amongst the organic compounds we have studied so far. However, compared to mineral acids these are quite weak. In aqueous solutions carboxylic acids exist in equilibrium with carboxylate and hydronium ions.

$$RCOOH + H_2O \rightleftharpoons RCOO^- + H_3O^+$$

The equilibrium constant for this system is called acidity constant, K_a, of the acid and is given by the expression :

$$K_a = \frac{[RCOO^-][H_3O^+]}{[RCOOH]}$$

(Concentration of water is omitted because as a solvent it is present in a large excess and its concentration remains essentially constant). Each acid has its characteristic acidity constant, K_a; the larger the value of K_a, the stronger is the acid. K_a values of some acids are given in Table 17.1

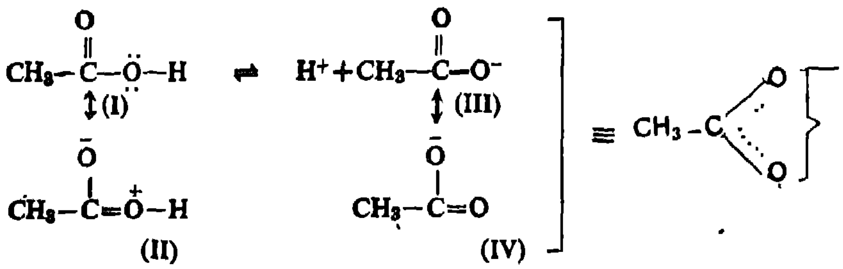
TABLE 17.1

K_a Values of Some Acids

Formula	*Name*	*K_a*
$HCOOH$	formic acid	17.7×10^{-5}
CH_3COOH	acetic acid	1.75×10^{-5}
$ClCH_2COOH$	chloroacetic acid	136×10^{-5}
$Cl_2CHCOOH$	dichloroacetic acid	5530×10^{-5}
Cl_3CCOOH	trichloroacetic acid	23300×10^{-5}
FCH_2COOH	fluoroacetic acid	260×10^{-5}
$BrCH_2COOH$	bromoacetic acid	125×10^{-5}
ICH_2COOH	iodoacetic acid	67×10^{-5}

Let us see why carboxylic acids ionize to give hydrogen ions, whereas alcohols, which also have hydroxyl groups like the acids, are neutral substances. The ionization in the two cases can be represented as follows :

$$CH_3{-}CH_2 \rightarrow O{-}H \rightleftharpoons CH_3{-}CH_2 \rightarrow O^- + H^+$$



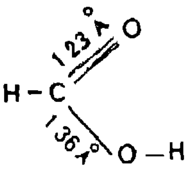
Non-equivalent structures I and II less resonance stabilization

Equivalent stuctures III and IV more resonance stabilization

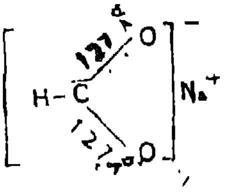
The alcohol and alkoxide ion are each represented by single structures only. The alkoxide ion is destablized by the inductive effect of the alkyl group which tends to increase the charge density on the oxygen atom. On the other hand, both the acid and the carboxylate ion are each resonance hybrids. However, in the case of the acid the two reasonance structures are non-equivalent and, therefore, less important structure II actually involves separation of charges between two similar atoms. The carboxylate ion has two equivalent resonance structures and therefore, it is much more resonance stabilized than the acid. The higher stability of the carboxylate ion shifts the equilibrium towards further ionization.

That the carboxylate ion is indeed a resonance hybrid is supported by measurement of bond lengths in formic acid and in sodium formate by X-ray and electron diffraction methods.

Formic acid contains one carbon-oxygen bond of 1.36 Å (single bond) and another of 1.23 Å (double bond); whereas in sodium formate both carbon-oxygen bonds are equal and 1.27 Å in length.



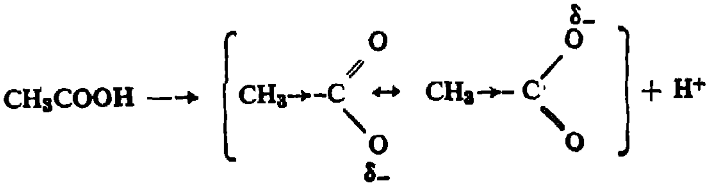
formic acid

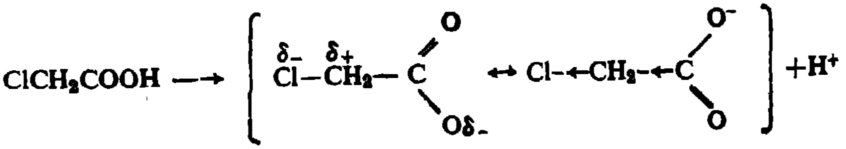


sodium formate

Effect of substituents on acidity of acids :

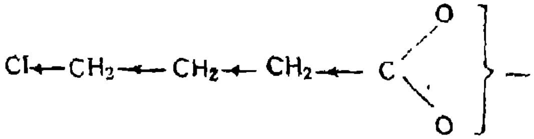
As the figures in Table 17.1 show, chloroacetic acid is about 100 times stronger than acetic acid. To explain this we should compare the relative stabilities of the anions of these two acids.





In acetic acid, the electron donating effect of methyl group destablizes the anion (acetic acid has a much lower K_a value than formic acid). In the case of chloroacetic acid, on the other hand electron withdrawing effect of chlorine stablizes the anion due to dispersal of charge favouring a higher degree of ionization In general, electron donating substituents have an acid weakening effect and electron withdrawing substituents, have an acid strengthening effect. Table 17.1 also shows that dichloroacetic acid is a stronger acid than monochloroacetic acid and trichloroacetic acid is almost as strong as a mineral acid.

Fluoroacetic acid is stronger than chloroacetic acid and both bromo and iodoacetic acids are weaker than chloroacetic acid. We can thus predict the relative strengths of the halogenated acids on the basis of attractions of halogens for electrons. Since this influence decreases very rapidly with distance of halogen from the carboxylic group, it becomes almost ineffective when acting through four or more carbon atoms in a chain.



The effect of halogen substitution on acid strength is more marked if the substituent is on α-carbon (closer) K_a values for the two chlorobutanoic acids support this hypothesis.

$CH_3CH_2CHClCOOH$	$ClCH_2CH_2CH_2COOH$
$K_a = 139 \times 10^{-5}$	$K_a = 2.96 \times 10^{-5}$

Benzonic acid ($K_a = 6.5 \times 10^{-5}$) is somewhat stronger than simple aliphatic acids. Here the carboxylate group is attached to a more electronegative carbon (sp^2 hybridized) than in aliphatic acids (sp^3 hybridized).

The carboxylic acids react with alkalies to form salts. Mineral acids convert these salts back into original acids.

$$\underset{\text{acid molecule}}{RCOOH} \quad \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} \quad \underset{\text{salt anion}}{RCOO^-}$$

The salts of carboxylic acids are ionic compounds. They are non-volatile solids and generally decompose before melting The alkali metal salts of carboxylic acids (sodium, potassium and ammonium) are soluble in water and insoluble in non-polar solvents. Thus carboxylic acids (except first four which are soluble in water) and their salts have exactly opposite solubility behaviour. This difference can be used to identify an acid and also to separate it from non-polar or basic substances. A water insoluble organic compound that dissolves in dilute sodium hydroxide must either be a carboxylic acid or a weakly acidic phenol

$$\underset{\text{insoluble in water}}{RCOOH} + NaOH \longrightarrow \underset{\text{water soluble salt}}{RCOONa} + H_2O$$

Phenols and acids can be differentiated by using a solution of $NaHCO_3$ instead of sodium hydroxide Sodium bicarbonate solution reacts with and dissolves acids forming bubbles of CO_2 but it does not react with most phenols.

$$RCOOH + NaHCO_3 \longrightarrow RCOONa + H_2O + CO_2$$

Carboxylic acids also react with metals like zinc and magnesium evolving hydrogen.

$$2CH_3COOH + Zn \longrightarrow (CH_3COO)_2Zn + H_2$$

Since ionizable hydrogen comes only from the carboxylic group of an acid, monocarboxylic acids are also monobasic in nature.

2 *Reduction* : Carboxylic acids can be reduced to primary alcohols with lithium aluminium hydride.

$$RCOOH \xrightarrow{LiAlH_4} RCH_2OH$$

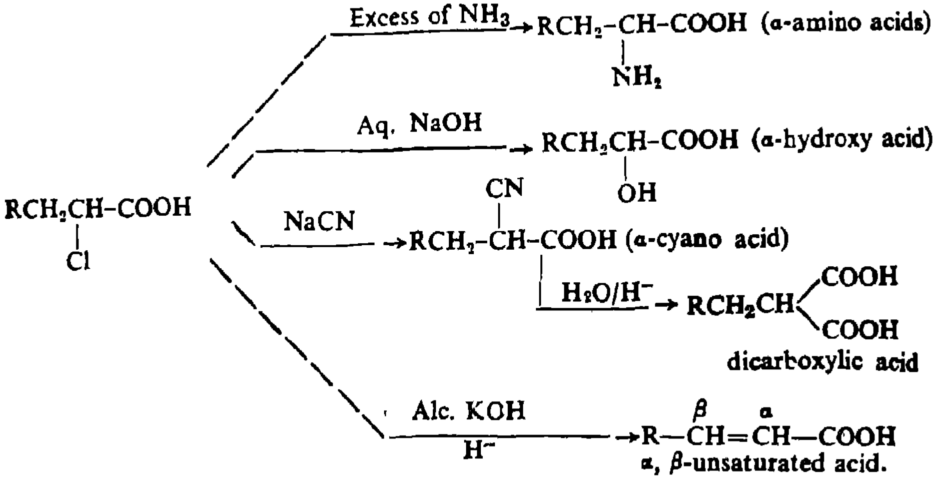
3. *Conversion into functional derivatives* : Acid chlorides, anhydrides, esters and amides are called functional derivatives of carboxylic acids. All these derivatives are formed by replacement of the —OH of the carboxyl group. The details about their preparation and reactions would be discussed in the next section.

4. *Alpha halogenation of aliphatic acids* : Alpha hydrogens of carboxylic acids can be replaced by chlorination or bromination in the presence of a small amount of phosphorous acting as catalyst. This reaction is known as *Hell-Vohlard-Zelinsky reaction.*

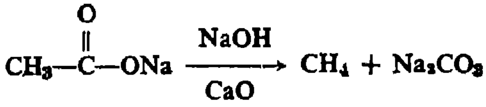
$$CH_3COOH \xrightarrow{Cl_2/P} ClCH_2COOH \xrightarrow{Cl_2/P} Cl_2CHCOOH \xrightarrow{Cl_2/P} Cl_3CCOOH$$

If more than one mole of chlorine or bromine is used, the second and third hydrogens at α-position may be successively replaced. This mode of halogenation is specific for alpha position only.

The reaction has large synthetic utility because a halogen can be substituted smoothly by a number of groups to give various new and useful products.

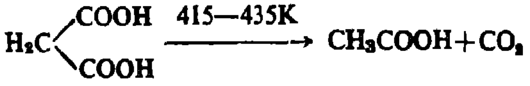


5. *Decarboxylation*: The conditions for decarboxylation (removal of CO_2) of a carboxylic acid depend upon its nature Some acids get decarboxylated when their sodium salts are heated with sodalime (NaOH-CaO).



$$CH_3-\overset{\overset{O}{\|}}{C}-ONa \xrightarrow[CaO]{NaOH} CH_4 + Na_2CO_3$$

When two carboxyl groups are attached to the same carbon atom, decarboxylation can take place simply on heating.



$$H_2C(COOH)_2 \xrightarrow{415-435K} CH_3COOH + CO_2$$

malonic acid

Conditions under which decarboxylation is carried out also determine the nature of the products formed. For example, when calcium salts of carboxylic acids are heated, ketones are formed. Heating a mixture of calcium salt of a carboxylic acid with calcium formate gives an aldehyde.

$$(CH_3COO)_2Ca \xrightarrow{heat} CH_3COCH_3 + CaCO_3$$

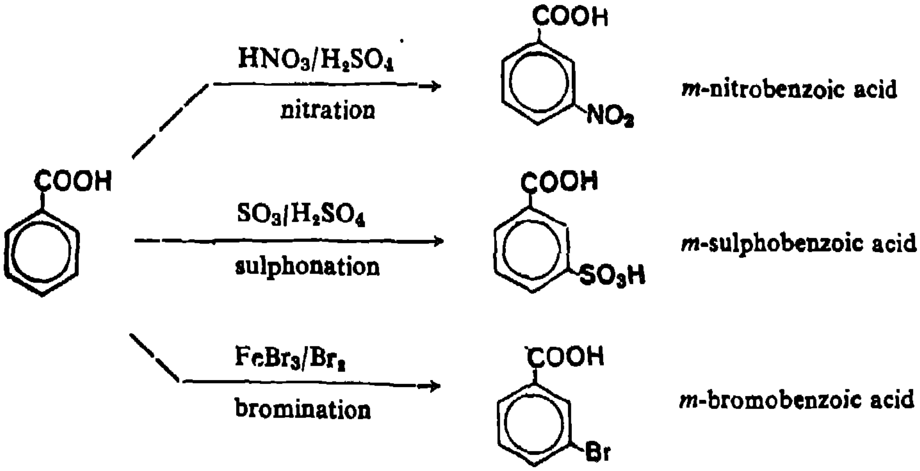
$$(CH_3COO)_2Ca + (HCOO)_2Ca \xrightarrow{heat} 2CH_3CHO + 2CaCO_3$$

Alkali salts of carboxylic acids undergo decarboxylation on electrolysis.

$$2CH_3COO^-K^+ \xrightarrow[H_2O]{\text{electrolysis}} \begin{cases} \rightarrow CH_3-CH_3+2CO_2 \text{ (at anode)} \\ \rightarrow 2KOH+H_2 \quad \text{(at cathode)} \end{cases}$$

Kolbe used this method for preparing alkanes from carboxylic acids.

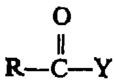
6. *Ring substitution in aromatic acids :* Carboxyl group in benzoic acid is an electron withdrawing group and therefore it is *m*-directing.



Substitution reactions of benzoic acid give mostly meta-substituted products.

17.5 FUNCTIONAL DERIVATIVES OF ACIDS

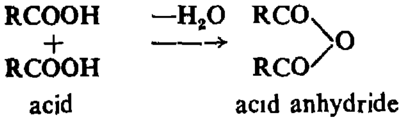
Functional derivatives of carboxylic acids are obtained by replacement of the OH part of —COOH group by other groups. These compounds may be given the general formula.



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-Y$$

where R is an alkyl or an aryl group and Y is a replacement for the OH group.

When Y is one of the halogen atoms, we get *acid* or *acyl halides* ($R-\overset{\overset{O}{\|}}{C}-Y$ when Y is amino group, we get *acid amides* ($R-\overset{O}{\overset{\|}{C}}-NH_2$). Replacement of the OH part of carboxylic group by an alkoxy group derived from an alcohol gives an *ester* ($R-\overset{O}{\overset{\|}{C}}-OR$) Loss of a water molecule between the two OH groups of two acid molecules yields an ***acid anhydride.***



17.5-1 NOMENCLATURE

These acid derivatives are named according to the common or the IUPAC name of the corressponding carboxylic acid Table 17.2 (on page 281) describes the nomenclature of various derivatives of acids.

17.5-2 PHYSICAL PROPERTIES

The functional derivatives of acids are also polar compounds. However, hydrogen bonding not being possible in esters, acid anhydrides and acid chlorides, they remain as unassociated molecules The boiling points of esters and acid chlorides are accordingly lower than those of the corresponding acids However, the anhydrides boil at higher temperatures than the corresponding acids as their molecular masses are almost double. The same consideration applies to esters if the alkyl group from the alcohol is a large one. Amongst acid derivatives, amides alone are capable of forming strong intermolecular hydrogen bonds and are generally solids at room temperature. They have high boiling points Table 17.3 shows a comparison of the melting and boiling points of some acid derivatives.

TABLE 17.3

Melting and Boiling Points of Some Acids and Their Chlorides, Anhydrides, Amides and Esters (K)

	Acid	*Acid chloride*	*Acid anhydride*	*Methyl ester*	*Amide*
Acetic Acid					
m. p.	289.6	161	200	175.0	355
b. p.	391.0	324	413	330.5	494
Benzoic acid					
m. p.	395	272	315	258	403
b. p.	522	470	633	471-473	563

TABLE 17.2

Common and the IUPAC Names of Functional Derivatives of Acids

	Acids	*Acid or acyl chlorides*	*Acid anhydrides*	*Acid amides*	*Methyl esters*
Formula	$CH_3-\overset{O}{\overset{\|}{C}}-OH$	$CH_3-\overset{O}{\overset{\|}{C}}-Cl$	$CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3$	$CH_3-\overset{O}{\overset{\|}{C}}-NH_2$	$CH_3-\overset{O}{\overset{\|}{C}}-OCH_3$
Common name	Acetic acid	Acetyl chloride	Acetic anhydride	Acetamide	Methyl acetate
IUPAC name	Ethanoic *acid*	Ethano*yl* chloride	Ethanoic *anhydride*	Ethan*amide**	Methyl ethan*oate*
Formula	$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-OH$	$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-Cl$	$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_2-CH_3$	$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-NH_2$	$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-OCH_3$
Common name	Propio*nic acid*	Propio*nyl chloride*	Propionic *anhydride*	Propion*amide*	Methyl propion*ate*
IUPAC name	Propan*oic acid*	Propano*yl chloride*	Propanoic *anhydride*	Propan*amide*	Methyl propan*oate*
Formula	$C_6H_5-\overset{O}{\overset{\|}{C}}-OH$	$C_6H_5-\overset{O}{\overset{\|}{C}}-Cl$	$C_6H_5-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-C_6H_5$	$C_6H_5\overset{O}{\overset{\|}{C}}-NH_2$	$C_6H_5-\overset{O}{\overset{\|}{C}}-OCH_3$
Common name	Benzoic acid	Benzo*yl chloride*	Benzoic *anhydride*	Benz*amide*	Methyl benzo*ate*
IUPAC name	Benz*oic acid*	Benzo*yl chloride*	Benzoic *anhydride*	Benzamide	Methyl benzoate

*In the IUPAC nomenclature, the acid amide are called alkanamides, the ending 'e' of the parent hydrocarbon being replaced by amide.

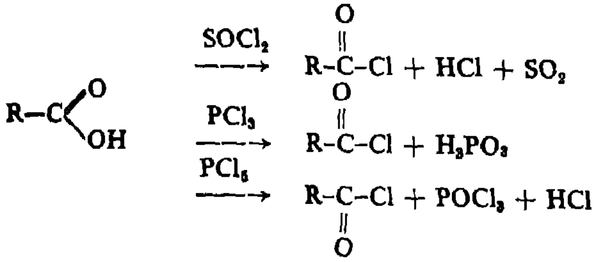
Functional derivatives of acids are soluble in common organic solvents Acid chlorides and anhydrides are readily decomposed by water. In fact acid chlorides are difficult to handle as they start fuming in humid atmosphere Esters have very low solubility in water, amides are more soluble in water than the other derivatives due to their association with water through hydrogen bonding.

Esters have pleasant fruity odours and are often used in the preparation of synthetic perfumes and essences. Acid chlorides and anhydrides have sharp irritating odours and induce watering from eyes and nose.

17.5-3 PREPARATION

The functional derivatives of acids can be prepared from the corresponding carboxylic acids, but some as shown below, are more conveniently obtained through other reactions

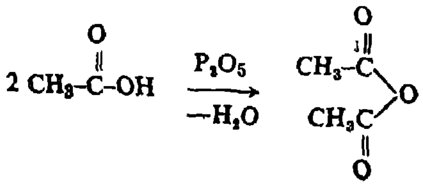
Acid Chlorides : These are prepared from carboxylic acids by treatment with reagents which replace an –OH group by –Cl, e.g. thionyl chloride, phosphorous trichlorides or phosphorus pentachloride.



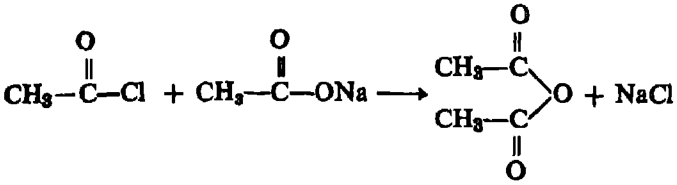
R may be any alkyl or aryl group

Thionyl chloride is generally preferred, because by products being gaseous, it is easy to purify the acid chloride formed.

Acid Anhydrides : As the name implies, anhydrides are formed by loss of a water molecule from two molecules of carboxylic acid. This can be brought about by heating an acid with a strong dehydrating agent like phosphorus pentoxide :

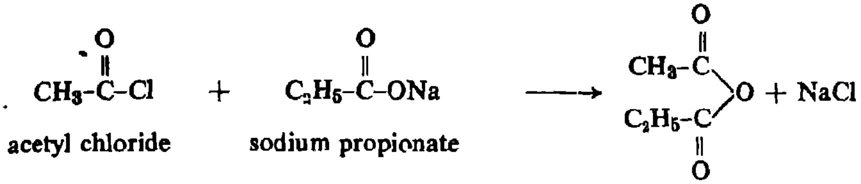


Another method of their preparation is by reaction of an acid chloride with sodium salt of the acid. Mixed anhydrides may also be obtained in this way.



$$CH_3-\overset{O}{\overset{\|}{C}}-Cl + CH_3-\overset{O}{\overset{\|}{C}}-ONa \longrightarrow (CH_3CO)_2O + NaCl$$

acetic anhydride

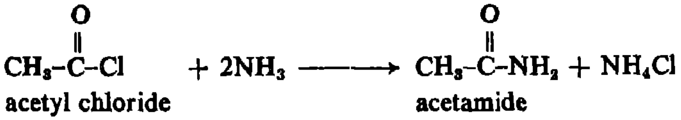


$$CH_3-\overset{O}{\overset{\|}{C}}-Cl + C_2H_5-\overset{O}{\overset{\|}{C}}-ONa \longrightarrow CH_3CO-O-COC_2H_5 + NaCl$$

acetyl chloride sodium propionate

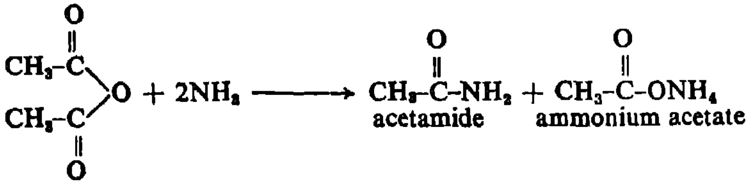
acetic propionic anhydride

Amides : Most convenient method for preparing amides is reaction of ammonia with esters, anhydrides or acid chlorides. In these reactions, acid chlorides react vigorously, anhydrides readily and esters rather slowly.



$$CH_3-\overset{O}{\overset{\|}{C}}-Cl + 2NH_3 \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-NH_2 + NH_4Cl$$

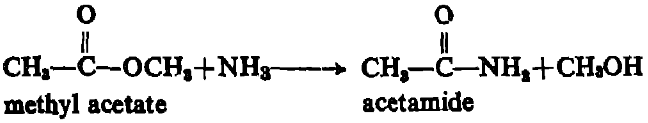
acetyl chloride acetamide



$$(CH_3CO)_2O + 2NH_2 \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-NH_2 + CH_3-\overset{O}{\overset{\|}{C}}-ONH_4$$

acetamide ammonium acetate

acetic anhydride



$$CH_3-\overset{O}{\overset{\|}{C}}-OCH_3+NH_3 \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-NH_2+CH_3OH$$

methyl acetate acetamide

Partial hydrolysis of nitriles with alkaline hydrogen peroxide also gives amides.

$$CH_3CN + 2\ H_2O_2 \xrightarrow{OH^-} CH_3CONH_2 + H_2O + O_2$$

acetonitrile acetamide

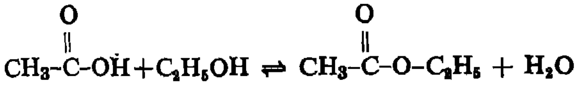
In industry amides are prepared by thermal decomposition of ammonium salts of carboxylic acids.

$$CH_3COOH+NH_3 \longrightarrow CH_3COONH_4 \xrightarrow{\text{catalyst}} CH_3CONH_2+H_2O$$

ESTERS

Esters may be prepared by acylation of alcohols or phenols using acids, acid chlorides or anhydrides.

Carboxylic acids, react with alcohols under dehydration conditions provided by mineral acids. The reaction is called *esterification.* It is a reversible reaction; the equilibrium is generally reached when appreciable quantities of both reactants and products are present



$$CH_3-\overset{\overset{\Large O}{\|}}{C}-OH+C_2H_5OH \rightleftharpoons CH_3-\overset{\overset{\Large O}{\|}}{C}-O-C_2H_5 + H_2O$$

ethyl acetate

In esterification of acetic acid with ethyl alcohol (equation given above), when one mole each of acetic acid and ethyl alcohol are heated in the presence of a little concentrated sulphuric acid, equilibrium is attained when 2/3 mole each of ester and water are formed and 1/3 mole each of acetic acid and alcohol are left unreacted. The reverse reaction of hydrolysis* of the ester into acid and alcohol is also acid catalyzed

To get good yields of esters, the equilibrium must, therefore, be shifted to the right. This can be achieved by taking an excess of alcohol and removing the water formed in the reaction. With a given acid, the relative rates of esterification by alcohols are in the order primary>secondary>tertiary. With a given alcohol, the relative rates of reaction with acids are in the order $RCH_2COOH>R_2CHCOOH>R_3CCOOH$.

Acid chlorides or anhydrides also react with alcohols or phenols to give esters. These reactions are fast and go to completion. An alkali or a tertiary amine is used in the case of acid chlorides to neutralize the hydrochloric acid formed

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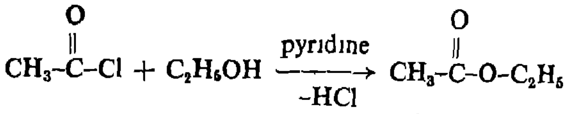
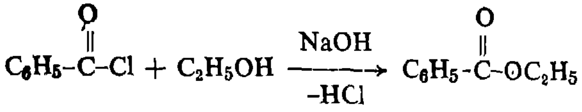
* Alkaline hydrolysis of esters is also called *saponification*. As we shall see later oils and fats which are glyceryl esters of higher fatty acids give soaps on alkaline hydrolysis.



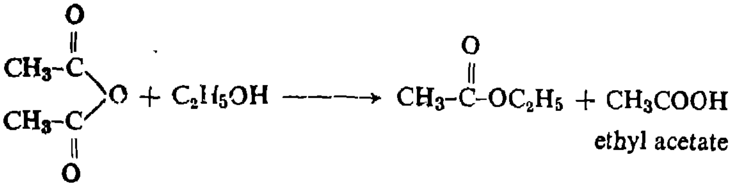
$$CH_3-\overset{O}{\overset{\|}{C}}-Cl + C_2H_5OH \xrightarrow[-HCl]{\text{pyridine}} CH_3-\overset{O}{\overset{\|}{C}}-O-C_2H_5$$

ethyl acetate



$$C_6H_5-\overset{O}{\overset{\|}{C}}-Cl + C_2H_5OH \xrightarrow[-HCl]{NaOH} C_6H_5-\overset{O}{\overset{\|}{C}}-OC_2H_5$$

ethyl benzoate



$$(CH_3CO)_2O + C_2H_5OH \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-OC_2H_5 + CH_3COOH$$

ethyl acetate

17.5-4 CHEMICAL REACTIONS

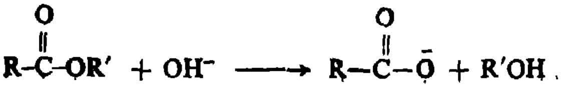
The characteristic reactions of functional derivative of carboxylic acids are replacement reactions. The $-Cl$, $-O-\overset{O}{\overset{\|}{C}}-R$, $-NH_2$, or $-OR$ groups can be replaced by some others.

Hydrolysis of acid derivatives : These derivatives can be hydrolysed more easily in alkaline or acidic media than in water alone.

The details of the acid and base catalyzed hydrolysis of esters are described below. As pointed out earlier, acid hydrolysis of esters is reversible, and leads to an equilibrium mixture of reactants and products.

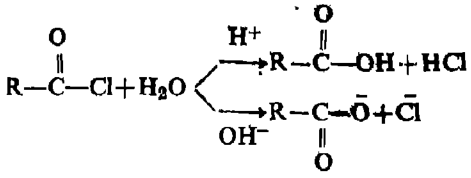
$$RCOOR + H_2O \underset{\text{esterification}}{\overset{(H^+)\text{ hydrolysis}}{\rightleftharpoons}} RCOOH + ROH$$

The base catalyzed hydrolysis of an ester is essentially irreversible.

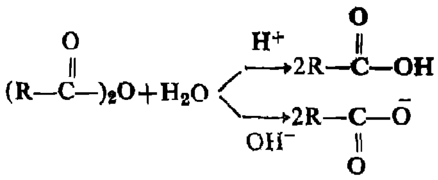


$$R-\overset{O}{\overset{\|}{C}}-OR' + OH^- \longrightarrow R-\overset{O}{\overset{\|}{C}}-\bar{O} + R'OH$$

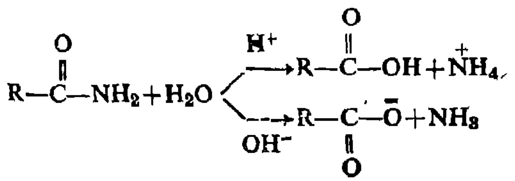
Hydrolysis of acid chlorides, anhydrides and amides proceeds in similar manner with the formation of HCl, carboxylic acids and ammonia respectively.



$$R-\overset{O}{\overset{\|}{C}}-Cl+H_2O \xrightarrow{H^+} R-\overset{O}{\overset{\|}{C}}-OH+HCl$$
$$R-\overset{O}{\overset{\|}{C}}-Cl+H_2O \xrightarrow{OH^-} R-\underset{O}{\underset{\|}{C}}-\bar{O}+\bar{Cl}$$



$$(R-\overset{O}{\overset{\|}{C}}-)_2O+H_2O \xrightarrow{H^+} 2R-\overset{O}{\overset{\|}{C}}-OH$$
$$(R-\overset{O}{\overset{\|}{C}}-)_2O+H_2O \xrightarrow{OH^-} 2R-\underset{O}{\underset{\|}{C}}-\bar{O}$$

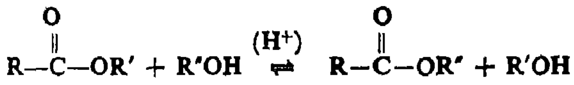


$$R-\overset{O}{\overset{\|}{C}}-NH_2+H_2O \xrightarrow{H^+} R-\overset{O}{\overset{\|}{C}}-OH+\overset{+}{N}H_4$$
$$R-\overset{O}{\overset{\|}{C}}-NH_2+H_2O \xrightarrow{OH^-} R-\underset{O}{\underset{\|}{C}}-\bar{O}+NH_3$$

Alcoholysis

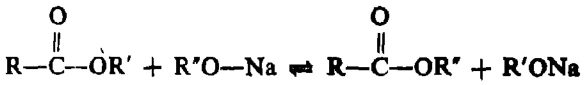
We have already seen that acid chlorides and anhydrides react with alcohols to form esters. The reaction of an ester with an alcohol is called *trans-esterification.* This reaction is catalyzed by acids (H_2SO_4 or HCl) or bases (usually alkoxide ions). The mechanism of trans-esterification reaction is similar to that of esterification.

Acid-catalyzed



$$R-\overset{O}{\overset{\|}{C}}-OR' + R'OH \overset{(H^+)}{\rightleftharpoons} R-\overset{O}{\overset{\|}{C}}-OR' + R'OH$$

Base-catalyzed

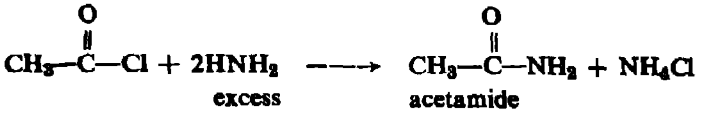


$$R-\overset{O}{\overset{\|}{C}}-OR' + R'O-Na \rightleftharpoons R-\overset{O}{\overset{\|}{C}}-OR' + R'ONa$$

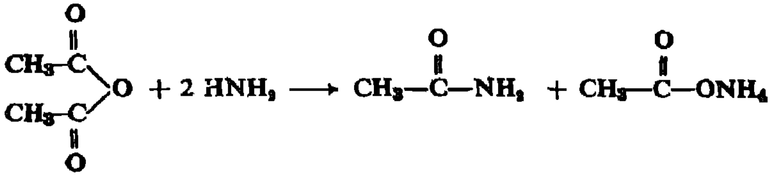
Trans-esterification is an equilibrium reaction. It is, therefore, necessary to use a large excess of alcohol of which we wish to prepare the new ester, or we have to remove one of the products of reaction to carry this reaction to completion.

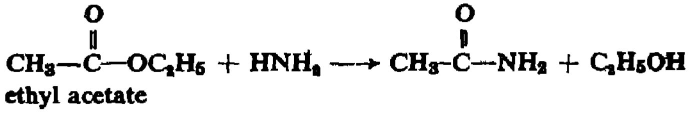
Ammonolysis

Reaction of ammonia with acid chlorides, anhydrides or esters leads to the formation of amides :



$$CH_3-\overset{\overset{\Large O}{\|}}{C}-Cl + \underset{\text{excess}}{2HNH_2} \longrightarrow \underset{\text{acetamide}}{CH_3-\overset{\overset{\Large O}{\|}}{C}-NH_2} + NH_4Cl$$





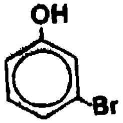
$$\underset{\text{ethyl acetate}}{CH_3-\overset{\overset{\Large O}{\|}}{C}-OC_2H_5} + HNH_2 \longrightarrow CH_3-\overset{\overset{\Large O}{\|}}{C}-NH_2 + C_2H_5OH$$

As we shall see in the next unit, primary and secondary amines can take the place of ammonia in such reactions. Then we get substituted amides as the products.

EXERCISES

17.1 Write the IUPAC names of the following compounds :

$ClCH_2\,CH_2\,CHOHCH_3$, $O-CH_3C_6H_4OH$,



$,H_3COCH_2CH_2COOH$,

p-Br $C_6H_4OC_2H_5$, $CH_3OCH\,(CH_3)_2$, $C_6H_5CH_2COOH$, $(CH_3)_3\,CCOOH$,

$(CH_3)_2CBr-\underset{\underset{\Large CH_2CH_3}{|}}{C}OHCH_3$, *m*-$OCH_3\,C_6H_4CHO$

$C_6H_5COCH_2CH_2CH_2CHCH_2CHO$, $H_5C_2O-\underset{\underset{\Large O}{\|}}{C}-H$

$C_6H_5COOCH\,(CH_3)_2$, $CH_3-\underset{\underset{\Large CH_3}{|}}{CH}-CONH_2$, $(C_6H_5CO)_2O$, $C_6H_5CONH_2$;

17.2 (i) Draw structures of eight isomeric pentyl alcohol $C_5H_{11}OH$, name each of alcohol according to IUPAC system and indicate each as primary, secondary and tertiary alcohol;

(ii) Give structures and IUPAC names of (a) nine isomeric esters of formula $C_5H_{10}O_2$ (b) seven carbonyl compounds of the formula $C_5H_{10}O$

17.3 Illustrate the following terms :

Grignard reagent, Dow process, Protonation, Oxonium ions, Absolute alcohol, Denatured alcohol, Methylated spirit, Power alcohol, Rosenmund reduction, Kolbe's reaction, Reimer-Tiemann reaction, Formalin, Trioxane, Paraldehyde, Acetal, Protecting group, Tollen reagent, Benedict reagent, Fehling reagent, Williamson synthesis, Clemmensen reduction, Wolff-Kishner reduction, Aldol condensation, Cannizzaro reaction, Hell-Vohlard-Zelinsky reaction, Trans esterification.

17.4 Arrange compounds in each set according to specified order and give reasons for your answers :

(i) *Increasing* order of boiling points.

(a) C_2H_6, C_2H_5OH, $(CH_3)_2O$, CH_2OHCH_2OH.

(b) C_2H_6, C_2H_5OH CH_3CHO, CH_3COOH.

(c) 3-pentanol, n-pentane, 2, 2-dimethylpropanol, *n*-pentanol.

(d) CH_3 COCl, $(CH_3CO)_2O$, CH_3CONH_2, CH_3COOH.

(ii) Increasing order of solubility in water.

$C_6H_5CHOHCH_3$, $C_6H_5CH_2OCH_3$, $C_6H_5CH_2CH_2CH_3$, *p*-$CH_3C_6H_4COOH$, *p*-$OHC_6H_4CH_2OH$.

(iii) Increasing order of acidity.

(a) C_6H_5OH, C_6H_5COOH, $C_6H_5CH_2OH$.

(b) Butanoic acid, 2-bromobutanoic acid, 3-bromobutanoic acid.

(c) Benzoic acid, *p*-nitrobenzoic acid, *p*-methyl benzoic acid.

17.5 *Account for the following :*

(i) In reactions involving cleavage of carbon-oxygen bond of alcohols, some acid is added to facilitate the reaction.

(ii) The order of reactivity of halogen acids with alcohols is HI>HBr>HCl.

(iii) Phenols do not undergo substitution at the carbon of C — OH bond.

(iv) If an alcohol is treated with an excess of sulphuric acid at 423K no etherification takes place.

(v) In the preparation of aldehydes from primary alcohols by oxidation aldehyde is distilled out as it is formed.

(vi) To decrease the solubility of organic compound in water, sodium chloride is dissolved in water.

(vii) During distillation of old samples of ether, sometimes explosions occur

(viii) Phenyl methyl ether reacts with HI to give phenol and methyl iodide and not iodobenzene and methyl alcohol.

(ix) Dialkyl cadmium is used to prepare ketones from acid chlorides and not Grignard reagents.

(x) Oxidation of toluene to benzaldehyde with CrO_3 is carried out in acetic anhydride.

(xi) During the preparation of ammonia derivatives from carbonyl compound, pH of the reaction should be carefully controlled

(xii) Ammoniacal silver nitrate is used to oxidize aldehyde to corresponding carboxylic acid.

(xiii) In straight chain aliphatic carboxylic acids, one with even number of carbon atoms per molecule has a higher melting point than ones with odd numbers of carbon atoms immediately below and above it.

17.6 Discuss the method and chemical reactions involved in purification of carbonyl compounds by the bisulphite method.

17.7 How can alcohols, phenols and carboxylic acids be distinguished and separated from each other ?

17.8 How does Lucas reagent help in the distinction of primary, secondary and tertiary alcohol ? Discuss the reaction involved.

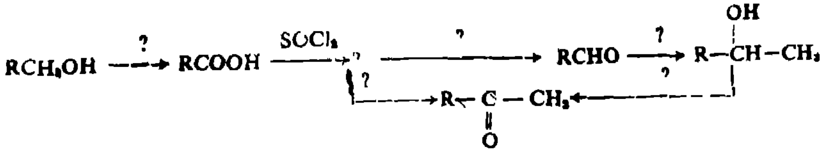
17.9 How is peroxide in ether detected and removed ?

17.10 Give tests to distinguish the following compounds and write the chemical equations involved $C_6H_5COCH_3$, $C_6H_5CH_2CHO$, $C_6H_5COCH_2CH_3$

17.11 Fill up the blanks.

(i) $RX \xrightarrow{Mg} ? \xrightarrow{CO_2} ? \xrightarrow{SOCl_2} ? \xrightarrow{NH_3} ?$

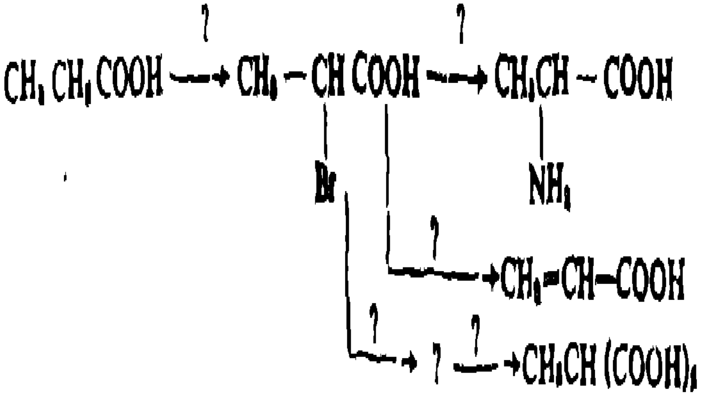
(ii)



(iii) $CH_3-CH=CH-CHO \xrightarrow[H^+]{(CH_2OH)_2} ? \xrightarrow{H_2/Ni} ? \xrightarrow[H_2O]{H^+} ?$

(iv) $RCH_2OH \xrightarrow{?} RCH_2Br \xrightarrow{?} RCH_2CN \xrightarrow{?} RCH_2COOH$

(v)



$CH_3CH_2COOH \xrightarrow{?} CH_3-\underset{Br}{CH}COOH \xrightarrow{?} CH_3\underset{NH_2}{CH}-COOH$

$CH_3-\underset{Br}{CH}COOH \xrightarrow{?} CH_2=CH-COOH$

$CH_3-\underset{Br}{CH}COOH \xrightarrow{?} ? \xrightarrow{?} CH_3CH(COOH)_2$

UNIT 18

Compounds with Functional Groups Containing Nitrogen

There are three main classes of organic compounds which contain nitrogen as a part of the functional group. These are:

(1) Cyanides, RCN or ArCN

(2) Nitro compounds, RNO_2

(3) Amines, RNH_2 or $ArNH_2$
R_2NH or Ar_2NH
R_3N or Ar_3N

18.1 CYANIDES AND ISOCYANIDES

These compounds are the derivatives of hydrogen cyanide, HCN. The functional group for this class of compounds is–CN. When the alkyl group is attached to the carbon atom of the CN group, we get the cyanides R–CN. When the attachment of the alkyl group is to nitrogen atom of CN group, we get the isocyanides, R–NC. Cyanides and isocyanides are isomeric compounds.

18.1-1 NOMENCLATURE

Alkyl cyanides are named by giving the name of alkyl group and adding the word cyanide to it. They are also named on the basis of acids produced on their hydrolysis. In this case the ending '–ic acid' of the acid is replaced by '–o–nitrile'. Thus, CH_3CN which yields acetic acid on hydrolysis is called acetonitrile.

In IUPAC system of nomenclature cyanides are called as *alkane nitriles.* The longest carbon chain containing the cyanide group is selected as the parent hydrocarbon. The carbon atom forming the part of CN group is also counted.

Some examples are given below to illustrate nomenclature of alkyl cyanides.

Molecular formula	*Trivial names*	*IUPAC names*
CH_3CN	methyl cyanide or acetonitrile	ethanenitrile
C_2H_5CN	ethyl cyanide or propionitrile	propanenitrile
C_3H_7CN	propyl cyanide or butyronitrile	butanenitrile
C_6H_5CN	phenyl cyanide or benzonitrile	benzonitrile

The isocyanides are named as alkyl isocyanides or alkyl isonitriles. Thus CH_3NC is methyl isocyanide or methyl isonitrile.

18.1-2 PREPARATION

(i) *From alkyl halides* : Alkyl cyanides are commonly prepared by the reaction of potassium or sodium cyanide with alkyl halides. The reaction is a nucleophilic substitution reaction, in which CN^- acts as the nucleophile The cyanide ion has an unshared pair of electrons on both ends : $C{\equiv}N^-$: . Therefore either carbon or nitrogen atom may act as the electron donor to the alkyl group. Alkyl cyanide is the chief product with potassium or sodium cyanide and isocyanide a minor product. With silver cyanide the chief product is the alkyl isocyanide. An anion like the cyanide ion, which may attack a given substrate molecule with either of its two attacking points (carbon or nitrogen atom in this case), giving rise to two different products is called as ambident nucleophile.

$$RX + (CN)^- - \begin{array}{l} \nearrow RCN \\ \searrow RNC \end{array}$$

(ii) *From acid amides* : Aryl and alkyl cyanides can also be prepared by dehydration of acid amides with P_2O_5 or $SOCl_2$. In fact this is a more suitable method, because no isocyanide is formed in this reaction.

$$CH_3CONH_2 \xrightarrow[-H_2O]{P_2O_5} CH_3CN$$

$$CH_3CONH_2 \xrightarrow{SOCl_2} CH_3CN + SO_2 + 2HCl$$

18.1-3 PHYSICAL PROPERTIES

-CN group is a highly polar group ; so is the $-NC$ group. As a result both the cyanides and the isocyanides have high dipole moments resulting in strong intermolecular attractions and high boiling points. A comparison with alkyl halides of comparable molecular mass would show this :

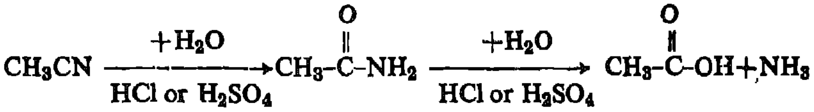
Compound	*Mol. Mass*	*b p.*
$CH_3-C\equiv N$	41	355
$CH_3-N \equiv C$	41	332
CH_3-Cl	50.5	249.3

Methyl cyanide is completely miscible with water. In general, solubility of these compounds in water decreases as we go up the homologous series. They are all soluble in non-polar solvents. The alkyl cyanides have generally pleasant odours whereas alkyl isocyanides have very disagreeable odours.

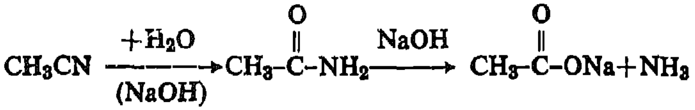
18.1-4 CHEMICAL PORPERTIES

There are two important types of reactions of nitriles i.e., hydrolysis and reduction.

(a) *Hydrolysis*: Nitriles can be hydrolysed both under acidic and basic conditions to give carboxylic acids and ammonia.



$$CH_3CN \xrightarrow[HCl\ or\ H_2SO_4]{+H_2O} CH_3-\overset{\overset{O}{\parallel}}{C}-NH_2 \xrightarrow[HCl\ or\ H_2SO_4]{+H_2O} CH_3-\overset{\overset{O}{\parallel}}{C}-OH+NH_3$$



$$CH_3CN \xrightarrow[(NaOH)]{+H_2O} CH_3-\overset{\overset{O}{\parallel}}{C}-NH_2 \xrightarrow{NaOH} CH_3-\overset{\overset{O}{\parallel}}{C}-ONa+NH_3$$

Under similar conditions isocyanides yield amines and formic acid.

$$RNC+2H_2O \xrightarrow[base]{acid\ or} RNH_2+HCOOH$$

(b) *Reduction*: Nitriles can be reduced catalytically by hydrogen in presence of Pt or Ni or chemically by reaction with sodium and ethyl alcohol. The product is the corresponding primary amine.

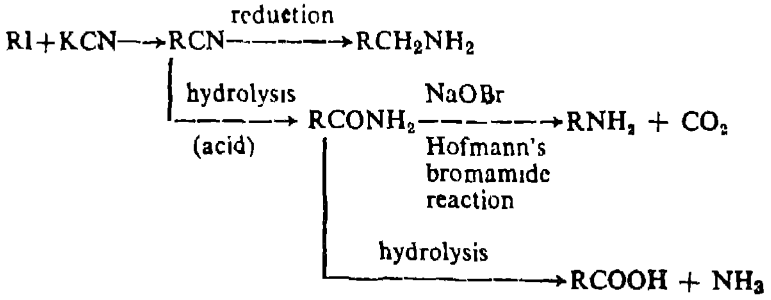
$$CH_3CN \xrightarrow[Na+C_2H_5OH]{H_2\ (Pt/Ni)} CH_3CH_2NH_2$$

Isocyanides on reduction yield secondary amines.

$$RNC \xrightarrow{H_2\ (Ni/Pt)} RNHCH_3$$

18.1-5 USES

Conversion of an alkyl halide to a cyanide results in the increase of one carbon atom in the molecule; so this provides a method of stepping up in series. The cyanides can be converted to amines or carboxylic acids as well as their derivatives Cyanides are, therefore, useful intermediates in organic synthesis. Following reactions illustrate some of these transformations :



$$RI + KCN \longrightarrow RCN \xrightarrow{\text{reduction}} RCH_2NH_2$$

$$RCN \xrightarrow[\text{(acid)}]{\text{hydrolysis}} RCONH_2 \xrightarrow[\text{Hofmann's bromamide reaction}]{NaOBr} RNH_2 + CO_2$$

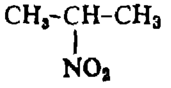
$$RCONH_2 \xrightarrow{\text{hydrolysis}} RCOOH + NH_3$$

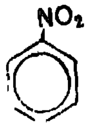
Vinyl cyanide or acrylonitrile, $CH_2{=}CHCN$, has a large scale commercial use in the production of nitrile rubbers and synthetic textiles.

18.2 NITROCOMPOUNDS

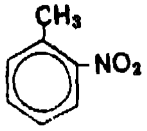
The functional group in these compounds is the nitro (NO_2 or $-N\genfrac{}{}{0pt}{}{\nearrow O}{\searrow O}$ group).

The aliphatic nitro compounds are called nitroalkanes and the aromatic ones, nitroarenes Examples of nomenclature :

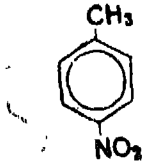
CH_3NO_2	nitromethane
$CH_3CH_2NO_2$	nitroethane
$CH_3CH_2CH_2NO_2$	1-nitropropane
 $CH_3\text{-}\underset{\substack{\vert \\ NO_2}}{CH}\text{-}CH_3$	2-nitropropane



nitrobenzene



o-nitrotoluene

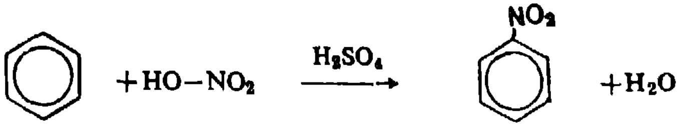


p-nitrotoluene

Isomeric compounds with the alkyl or aryl group attached to $-O-N=O$ group are called nitrites; thus $CH_3-O-N=O$ is named as methyl nitrite.

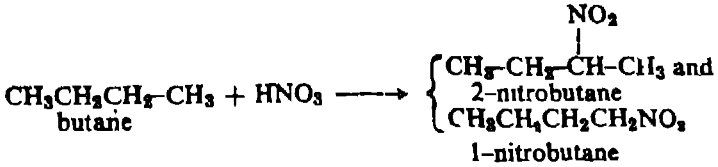
18.2-1 PREPARATION

Aromatic nitro compounds are easily prepared by nitration of the corresponding aromatic compound with HNO_3/H_2SO_4; a reaction discussed earlier (Part I, Sec. 18.7)



Such electrophilic aromatic substitution is facilitated by the presence of electron donating groups in the aromatic ring like the $-OH$ group (in phenol) or $-CH_3$ group (in toluene) and is made more difficult by electron withdrawing groups like $-NO_2$ (in nitrobenzene) or $-COOH$ (in benzoic acid).

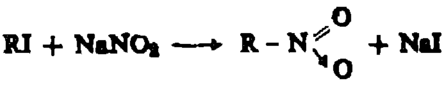
Aliphatic hydrocarbons do not undergo direct nitration so easily. High temperature nitration with nitric acid vapour gives lot of oxidation products along with some nitroalkanes. This is the commercial method for making nitroalkanes.



$$\underset{\text{butane}}{CH_3CH_2CH_2{-}CH_3} + HNO_3 \longrightarrow \begin{cases} CH_3{-}CH_2{-}\overset{NO_2}{CH}{-}CH_3 \text{ and} \\ \quad \text{2-nitrobutane} \\ CH_3CH_2CH_2CH_2NO_2 \\ \quad \text{1-nitrobutane} \end{cases}$$

$$+ \text{ oxidation products } (CO_2 + H_2O + NO_2, \text{ etc.})$$

Nitroalkanes can also be prepared by treating alkyl iodides with sodium nitrite. Treatment of an alkyl iodide with silver nitrite yields isomeric alkylnitrites in addition to nitroalkane.



$$RI + AgNO_2 \longrightarrow R-O-N=O + AgI$$

Nitrite ion (–O–N = O), like the cyanide (CN), is ambident. It has two points of attack. Attack by oxygen on the alkyliodide gives alkyl nitrites and attack by nitrogen gives nitroalkanes.

18.2-2 PHYSICAL PROPERTIES

Nitroparaffins or nitroalkanes are colourless liquids of agreeable odour They are sparingly soluble in water, but dissolve readily in organic solvents They are highly polar compounds and have higher boiling points than the hydrocarbons of comparable molecular masses. Nitroparaffins distil smoothly, whereas the isomeric alkyl nitrites explode on heating.

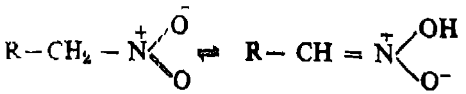
Aromatic nitrocompounds like nitrobenzene have generally a pale yellow colour. Nitrobenzene has a smell of bitter almonds. It has a high dipole moment and a high boiling point (483K). The aromatic nitrocompounds are not soluble in water; they are soluble in organic solvents.

18.2-3 CHEMICAL REACTIONS

(1) *Reduction* . The most important reaction of the nitrocompounds is their reduction to corresponding amines. This can be done by catalytic reaction with hydrogen in presence of Pt or Ni as well as by using strongly reducing mixtures like Fe, Sn or $SnCl_2$ with HCl.

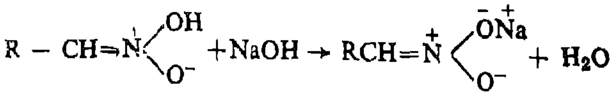
$$RNO_2 + 3H_2 \longrightarrow RNH_2 + 2H_2O$$

(2) *Salt formation* : Nitroalkanes exist in nitro form and aci isomeric forms.



nitroform aciform

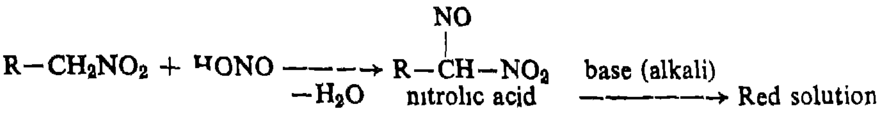
This phenomenon, involving reversible migration of a proton to give two very similar structural isomers in equilibrium with each other, is known as *tautomerism*. The isomers are named as tautomers (You have also studied this type of isomerism in Sec 18.4 of Part I.) Aci form is a weak acid and can form salts with strong bases.



Secondary nitroalkanes, R_2CHNO_2, can also tautomerise to *aci* forms but tertiary nitroalkanes, R_3C-NO_2 cannot. Therefore tertiary nitroalkanes do not form salts.

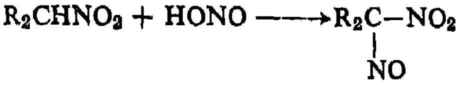
(3) *Reaction with nitrous acid* : The reaction with nitrous acid offers a method of distinguishing primary, secondary and tertiary nitroalkanes. A primary nitro-

alkane gives a nitroso-derivative. This has a tautomeric aciform called nitrolic acid which dissolves in an alkali to give a red solution.



$$R-CH_2NO_2 + HONO \xrightarrow[-H_2O]{} \underset{\text{nitrolic acid}}{R-\overset{\overset{NO}{|}}{C}H-NO_2} \xrightarrow{\text{base (alkali)}} \text{Red solution}$$

A secondary nitro compound reacts with nitrous acid to give a blue nitroso derivative. This cannot tautomerise to aci form and is insoluble in water as well as in an alkali.



$$R_2CHNO_2 + HONO \longrightarrow R_2\underset{\underset{NO}{|}}{C}-NO_2$$

blue colour

Tertiary nitroalkanes do not react with nitrous acid as there is no hydrogen atom on the carbon atom carrying the NO_2 group. They remain colourless and unchanged.

$R_3C-NO_2 + OHNO \longrightarrow$ no reaction

(4) *Hydrolysis* : The hydrolysis of primary nitroalkanes in presence of acids yields carboxylic acids and the salt of hydroxyl-amine.

$RCH_2NO_2 + HCl + H_2O \longrightarrow RCOOH + NH_2OH.HCl$

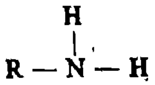
This method has been used for the commercial production of hydroxyl amine.

18.2-4 USES

Nitroalkanes have been used for the production of hydroxylamines, as solvents in plastics industry and as intermediates in production of explosives, detergents, medicines, etc. Most of the commercial chemical explosives are polynitro-compounds. Trinitro toluene (TNT) and trinitrobenzene are two of such explosives.

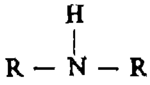
18.3 AMINES

Amines may be considered as amino derivatives of hydrocarbons or as alkyl derivatives of ammonia. The latter analogy suggests that one, two or all three hydrogen atoms in ammonia may be replaced by alkyl or aryl groups. Compounds corresponding to each of these possibilities are known They are classified as primary, secondary or tertiary amines according to the number of alkyl groups substituted into the ammonia molecule.



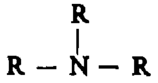
$R-\overset{\overset{H}{|}}{N}-H$

primary amine



$R-\overset{\overset{H}{|}}{N}-R$

secondary amine



$R-\overset{\overset{R}{|}}{N}-R$

tertiary amine

When one or more of the groups substituted into ammonia molecule is an aromatic ring, the amine is regarded as an aromatic amine e.g. $C_6H_5NH_2$ (aniline), $(C_6H_5)_2NH$ (diphenylamine), etc

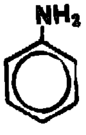
18.3-1 NOMENCLATURE

In the IUPAC system amines have been named by replacing the ending 'e' of alkanes by amine e g. CH_3NH_2 will be called methanamine. Amino group may also be treated as a substituent and the location of the amino group on the carbon chain is indicated by a number Thus we can have 1-aminopropane, or 2-aminopropane. Trivial names for the amines are obtained as *single words* by giving the name of the relevant alkyl group and adding the suffix amine Formulae and names of the first few primary amines are given below

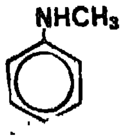
Compound	*Trivial name*	*IUPAC name*
CH_3NH_2	methylamine	aminomethane (methanamine)
$CH_3CH_2NH_2$	ethylamine	aminoethane (ethanamine)
$CH_3CH_2CH_2NH_2$	*n*-propylamine	1-aminopropane
$CH_3\underset{\underset{CH_3}{\vert}}{C}HNH_2$	*iso*-propylamine	2-aminopropane

Amines in general, and secondary and tertiary amines in particular are more often known by their trivial names.

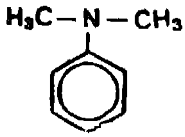
Aromatic amines are the compounds in which one or more aryl radicals are substituted in the ammonia molecule. These compounds are also generally named as derivatives of the simplest aromatic amine, aniline.



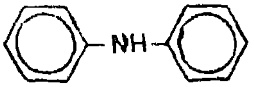
aniline
(primary amine)



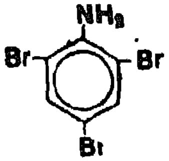
N—methylaniline
(secondary amine)



N, N—dimethylaniline
(tertiary amine)



Diphenylamine
(secondary amine)



2, 4, 6 – tribromoaniline
(primary amine)

18.3-2 PREPARATION

In the laboratory amines can be prepared by the following general methods.

(a) **From alkyl halides**

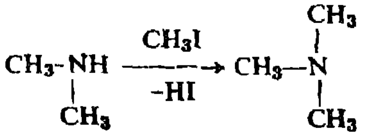
(i) By the action of ammonia—this type of reaction is called *ammonolysis*. An alkyl halide like methyl iodide can react with ammonia in the following way:

$$NH_3 + CH_3I \longrightarrow CH_3NH_2\,HI$$

$$CH_3NH_2.HI + NH_3 \longrightarrow CH_3NH_2 + NH_4I$$

The hydrogens of—NH_2 group may also get replaced by further alkyl groups in subsequent steps:

$$CH_3NH_2 \xrightarrow[-HI]{CH_3I} CH_3{-}NH{-}CH_3 \text{ (secondary amine)}$$



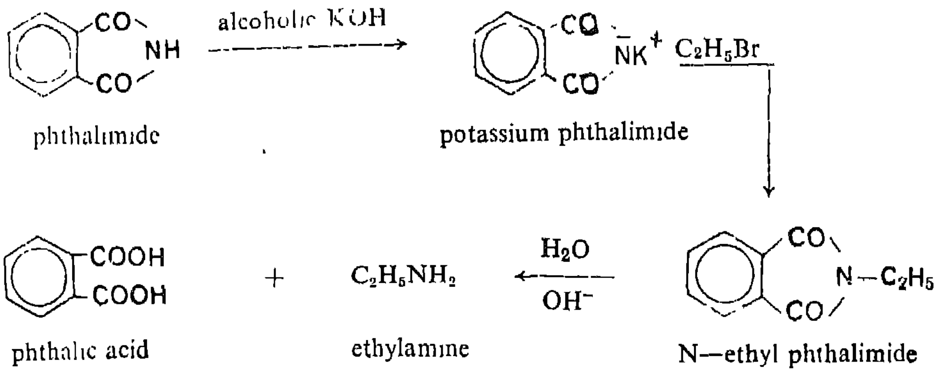
$$\underset{\displaystyle CH_3}{CH_3{-}\overset{}{N}H} \xrightarrow[-HI]{CH_3I} CH_3{-}\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{N}} \qquad \text{(tertiary amine)}$$

Another molecule of CH_3I will get added on the tertiary amine to form a quaternary ammonium iodide;

$$(CH_3)_3N + CH_3I \longrightarrow [(CH_3)_4N]^+\ I^-$$

The composition of the mixture obtained will depend on the ratio in which CH_3I and ammonia have been taken. However, the mixtures obtained are very complex and difficult to separate. This method is not of much practical value.

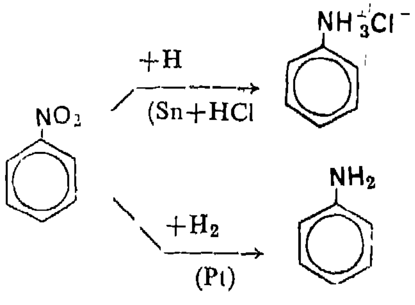
(ii) *Gabriel's synthesis*: Only primary amines can be prepared by this method. Following is the sequence of reactions for the synthesis of ethyl amine starting from phthalimide



Phthalic acid can be again converted to phthalimide and used repeatedly.

(b) From nitro-compounds, nitriles and amides by reduction

As we have seen, reduction of the nitro compounds can be carried out by using hydrochloric acid and a cheap metal like iron, zinc or tin Catalytic reduction with hydrogen in the presence of platinum or nickel is also possible.



This is the most important method for the preparation of primary amines especially aromatic primary amines, as aromatic nitro compounds are very easily obtained by nitration.

Alkyl cyanides can be reduced to give primary amines This reduction can be done catalytically as above, or by using sodium and ethanol

$$2C_2H_5OH + 2Na \longrightarrow 2C_2H_5ONa + 2H$$

$$CH_3CN \xrightarrow{+4H} CH_3CH_2NH_2$$

Isocyanides on similar reduction give secondary amines

$$CH_3NC \xrightarrow{+4H} CH_3NHCH_3$$

(c) **From amides by Hofmann bromamide reaction**

Acid amides when treated with bromine and alkali give primary amines e.g.,

$$CH_3CONH_2 \xrightarrow[\text{(or } Br_2 + NaOH)]{NaOBr} CH_3NH_2 + NaBr + CO_2$$

The CO_2 formed is absorbed by the NaOH present. It may be noted that he amide molecule has lost a carbon atom in the reaction. This reaction is called *Hofmann bromamide reaction* and provides a method for stepping down the series, since the amine would contain one carbon less than the acid amide taken.

13.3.3 INDUSTRIAL PREPARATION

Some of the simplest and the important amines are prepared on an industrial scale by processes that are not applicable as laboratory methods.

On an industrial scale, aliphatic amines like methylamine, dimethylamine and trimethylamine are prepared by passing mixed vapours of methanol and ammonia over alumina heated to 723K.

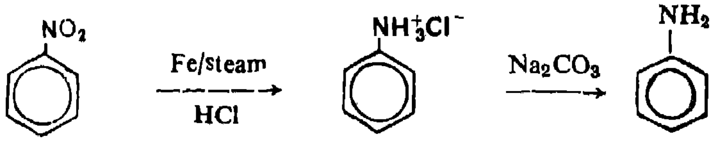
$$NH_3 \xrightarrow[Al_2O_3,723K]{CH_3OH} CH_3NH_2 \xrightarrow[Al_2O_3,\ 723K]{CH_3OH} (CH_3)_2NH \xrightarrow[Al_2O_3,723K]{CH_3OH} (CH_3)_3N$$

For the corresponding ethylamines ethanol and ammonia can be used.

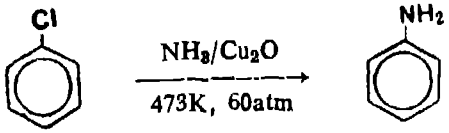
Aniline, the most important aromatic amine is prepared by the reduction of nitrobenzene with cheap reducing reagents like iron and steam in the presence of a small quantity of hydrochloric acid. The presence of the acid helps in the release of hydrogen from steam by iron. The acid is regenerated and keeps on cycling in the process.

$$Fe+2HCl \longrightarrow FeCl_2+2H$$

$$FeCl_2+2H_2O \longrightarrow Fe(OH)_2+2HCl$$

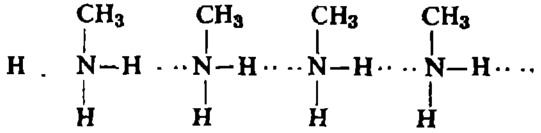


Chlorobenzene reacts with ammonia only at high temperatures and high pressures in the presence of a catalyst.



18.3-4 PHYSICAL PROPERTIES

Amines are polar compounds and, except tertiary amines, can form intermolecular hydrogen bonds.



$$H\,.\,\underset{H}{\overset{CH_3}{N}}-H\cdots\underset{H}{\overset{CH_3}{N}}-H\cdots\underset{H}{\overset{CH_3}{N}}-H\cdots\underset{H}{\overset{CH_3}{N}}-H\cdots$$

Amines therefore have higher boiling points than non-polar compounds of nearly the same molecular masses However, because of the lower electronegativity of nitrogen compared to oxygen, the hydrogen bonds in amines are weaker, and consequently their boiling points are lower than those of correspondidg alcohols or carboxylic acids.

Compounds	*Mol mass*	*b. p. (K)*
C_2H_6 (ethane)	30	184.5
CH_3NH_2 (methylamine)	31	265.5
CH_3OH (methyl alcohol)	32	333.0
HCOOH (formic acid)	46	374.0

Amines of all the three types are capable of forming hydrogen bonds with water. As a result lower aliphatic amines are soluble in water (methyl and ethyl amines are sold as 30% aqueous solutions) the higher ones with larger alkyl groups are less soluble; border line solubility being reached at about six carbon atoms in the molecule. Amines are also soluble in less polar solvents like benzene, ether, alcohol, etc. Aromatic amines are insoluble in water but soluble in benzene, ether and alcohol.

Ethyl and methyl amines smell like ammonia, higher amines have fishy odours. Aromatic amines are very toxic and are very easily oxidized by air and get coloured on keeping although they are colourless when pure and freshly prepared.

18.3-5 REACTIONS

Like ammonia, amines of all the three classes have an unshared pairs of electrons on the nitrogen atoms. Chemical properties of amines result from the tendency of nirogen atom to donate this pair of electrons to electron acceptors. Amines are thus basic compounds; they are much more basic than water Like ammonia they take up a molecule of water to form quaternary ammonium hydroxides. Basic powers of amines can be compared by measuring their dissociation constants, K_b.

$$RNH_3OH \rightleftharpoons RNH_3^+ + OH^-$$

$$K_b = \frac{[RNH_3^+][OH^-]}{[RNH_3OH]}$$

Each amine has its characteristic dissociation constant, K_b; the larger the value of K_b, the stronger the base. K_b values for ammonia and some amines are given below:

Compounds	K_b
NH_3	1.8×10^{-5}
CH_3NH_2	4.5×10^{-4}
$(CH_3)_2NH$	5.4×10^{-4}
$C_6H_5NH_2$	4.2×10^{-10}

The alkyl groups increase the availability of electrons on the nitrogen atom making these amines more basic than ammonia. On the other hand an aromatic ring attracts electrons from the nitrogen and greatly reduces its basic character

Chief among the substances which are deficient in electrons and which may accept electrons from the nitrogen atom of an amine are (i) protons, (ii) metal ions,

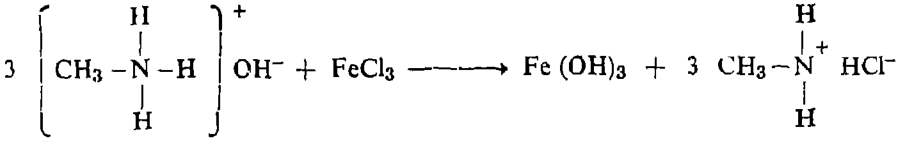
(iii) carbon atoms of low electron density, e.g. $>C=O$ group, and (iv) oxidizing agents Consequently the reactions of amines can be conveniently classified as follows.

(a) Protonation

(i) *Reaction of amines with water*: We have already seen above that amines react with water to give substituted ammonium and hydroxyl ions .

$$RNH_2+H_2O \longrightarrow R\overset{+}{N}H_3\overset{-}{OH} \rightleftharpoons RNH_3^+ + OH^-$$

The presence of OH^- ions in an aqueous solution of an amine is shown by precipitation of heavy metal hydroxides like $Fe(OH)_3$ on addition of a solution of $FeCl_3$:



$$3\left[CH_3-\underset{H}{\overset{H}{N}}-H\right]^+ OH^- + FeCl_3 \longrightarrow Fe(OH)_3 + 3\ CH_3-\underset{H}{\overset{H}{\overset{+}{N}}}\ HCl^-$$

(ii) *Reaction of amines with acids* Acids combine with amines to form substituted ammonium salts. Reaction of ethyl amines with hydrochloric acids is given below :

$$C_2H_5NH_2+HCl \longrightarrow C_2H_5NH_3^+ + Cl^-$$

Salts of amines are ionic compounds. They are non-volatile solids, and generally decompose before their melting points are reached They are soluble in water and insoluble in non-polar solvents. The amines, which are insoluble in watea, can be converted to the water soluble quaternary ammonium salts.

The difference between the solubility of an amine and its salt can be used to detect an amine and also to separate it from non polar substances A water insoluble nitrogen containing organic compound that dissolves in *cold dilute* hydrochloric acid can be taken to be an amine An amine can be separated from non-polar substances and water insoluble organic acids, taking advantage of its solubility in dilute mineral acids. After separation, amines can be regenerated by basifying the aqueous solution.

$$\underset{\text{water}}{C_6H_5NH_2} \underset{OH^-}{\overset{H^+}{\rightleftharpoons}} \underset{\text{water soluble}}{C_6H_5\overset{+}{N}H_3}$$

Basic nature of an amine can be used for its quantative estimation by titration with a standard solution of strong acid,

(iii) *Reaction of amines with nitrous acid* Nitrous acid reacts with amines differently than other acids. It gives straight forward salt formation with aliphatic tertiary amines but its reactions with aliphatic and aromatic primary and secondary amines are different Nitrous acid is unstable in more concentrated solution, therefore it is generated in presence of the amine from sodium nitrite using a mineral acid Reactions are carried out at low temperatures between 273 to 278 K.

Reaction of a primary amine with HNO_2

Primary aromatic amines react with nitrous acid to give diazonium salts

$$C_6H_5NH_2 + HONO \xrightarrow{\text{acid}} C_6H_5N_2OH + H_2O$$

$$C_6H_5N_2OH + HCl \longrightarrow C_6H_5\overset{+}{N}_2Cl^- + H_2O$$

Benzene diazonium chloride.

Aromatic diazonium compounds are very important synthetically and will be taken up in later section.

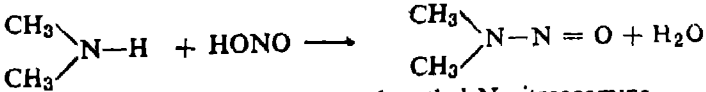
Primary aliphatic amines react with nitrous acid to give aliphatic diazonium compounds, these are unstable and decompose during the reaction to give alcohols.

$$CH_3NH_2 + HONO \longrightarrow CH_3N_2OH + H_2O$$

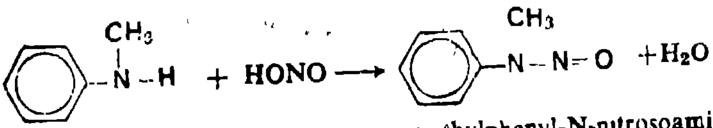
$$CH_3N_2OH \longrightarrow CH_3OH + N_2$$

Reaction of nitrous acid with secondary amines .

Secondary amines, both aliphatic and aromatic, react with nitrous acid to yield N-nitroso amines. These are yellow coloured neutral compounds insoluble in dilute aqueous mineral acids



dimethyl-N-nitrosoamine



methylphenyl-N-nitrosoamine

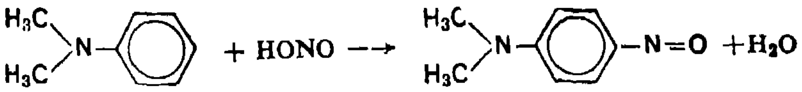
Reaction of tertiary amines with nitrous acid

Aliphatic tertiary amines form trialkyl ammonium nitrites with nitrous acid.

$$(CH_3)_3N + HONO \longrightarrow \left[(CH_3)_3\overset{+}{N}H\right]\overset{-}{NO_2}$$

trimethylammonium nitrite

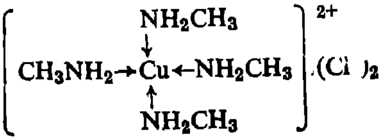
Due to very strong activation of the aromatic ring by an alkyl amine group, aromatic tertiary amines undergo substitution on the ring, generally in para position to give paranitroso compounds.



Introduction of $-N=O$ group in an aromatic ring is called *nitrosation*. The contrasting behaviour of amines towards nitrous acid may be used to differentiate the three classes of amines. Thus a primary aliphatic amines liberates a gas (N_2), a secondary amine gives a water-insoluble oil, sometimes yellow in colour, and a tertiary amine gives a water soluble salt.

(b) *Reactions of amines with metal ions*

Like ammonia amines form coordination compounds with metal ions like Ag^+ and Cu^{2+} Silver chloride dissolves in methylamine solution with formation of a complex salt, $[Ag(CH_3NH_2)]^+Cl^-$. Cupric chloride gives a deep blue complex with methylamine solutions, which has been assigned the structure :



$$\left[\begin{array}{c} NH_2CH_3 \\ \downarrow \\ CH_3NH_2\rightarrow Cu \leftarrow NH_2CH_3 \\ \uparrow \\ NH_2CH_3 \end{array}\right]^{2+} (Cl^-)_2$$

These complexes can be compared with the corresponding ones formed with ammonia.

(c) ***Reaction of amines with alkyl halides***

Amines react with alkyl halides much the same as ammonia does. Thus a primary amine can be converted to a secondary and tertiary amines and finally to a quaternary ammonium salts.

$$CH_3NH_2 + CH_3I \longrightarrow (CH_3)_2NH + HI$$

$$(CH_3)_2NH + CH_3I \longrightarrow (CH_3)_3N + HI$$
$$(CH_3)_3N + CH_3I \longrightarrow (CH_3)_4NI$$

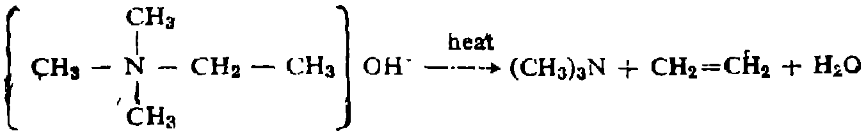
If the reaction with methyl iodide is carried out till a quaternary salt is produced, the process is called *exhaustive methylation.* The quaternary salts give quaternary ammonium bases when their aqueous solutions are treated with silver hydroxide.

In contrast to ammonium hydroxide, these quaternary bases are quite stable at ordinary temperatures. They are obtained as deliquescent solids when their solutions are evaporated to dryness in vacuum at low temperatures Quaternary ammonium bases are ionic in nature and are as basic as sodium and potassium hydroxides.

On heating, however, the quaternary ammonium bases decompose. Tetramethyl ammonium hydroxide gives trimethyl amine and methyl alcohol.

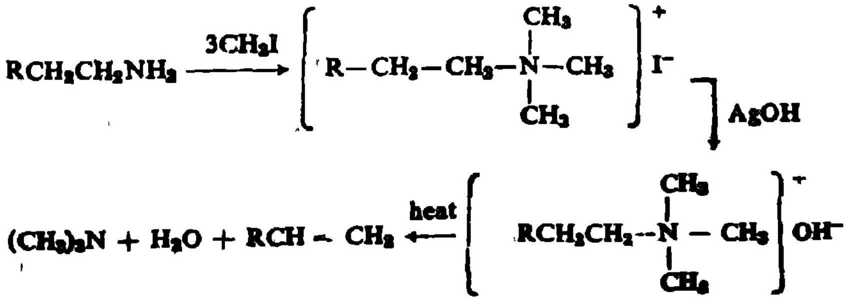
$$(CH_3)_4N^+OH^- \xrightarrow[389K]{heat} (CH_3)_2N + CH_3OH$$

But if one of the alkyl groups has two or more carbon atoms the products are a tertiary amine, an alkene and water, e.g. in the case of trimethyl ethyl ammonium hydroxide, the decomposition will be represented as .



$$\left[CH_3-\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large CH_3}{|}}{N}}-CH_2-CH_3\right]OH^- \xrightarrow{heat} (CH_3)_3N + CH_2{=}CH_2 + H_2O$$

This sequence of reactions forms the basis of Hofmann's method for deciding structures of unknown complex amines. The unknown amino compound is exhaustively methylated and converted into its quaternary base. Thermal decomposition of the latter gives a tertiary amine and an olefin From the structures of these two, especially the olefin, it is possible to deduce the structure of the parent amino compound. The number of moles of methyl iodide that react with one mole of the amino compound also indicates whether the amino group is primary, secondary or tertiary.

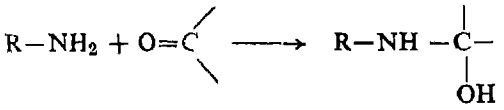


$$RCH_2CH_2NH_2 \xrightarrow{3CH_3I} \left[R-CH_2-CH_2-\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large CH_3}{|}}{N}}-CH_3\right]^+ I^- \;\downarrow AgOH$$

$$(CH_3)_3N + H_2O + RCH - CH_2 \xleftarrow{heat} \left[RCH_2CH_2-\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large CH_3}{|}}{N}}-CH_3\right]OH^-$$

(d) *Reactions of amines with compounds containing carbonyl groups*

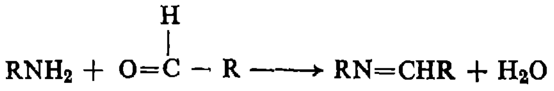
Amines act as nucleophiles towards compounds like aldehydes, acid chlorides and acid anhydrides. all of which have carbonyl groups The carbon of the carbonyl group is electron deficient and is susceptible to nucleophilic attack.



$$R{-}NH_2 + O{=}C\lessdot \longrightarrow R{-}NH{-}\overset{|}{\underset{\underset{OH}{|}}{C}}{-}$$

(i) *Reaction of primary amines with aldehydes*

Primary amines react with aldehydes to form Schiff's bases



$$RNH_2 + O{=}\overset{\overset{H}{|}}{C}-R \longrightarrow RN{=}CHR + H_2O$$

(Schiff's base)

In a typical reaction aniline reacts with benzaldehyde to give benzalaniline*. The reaction is exothermic and spontaneous.

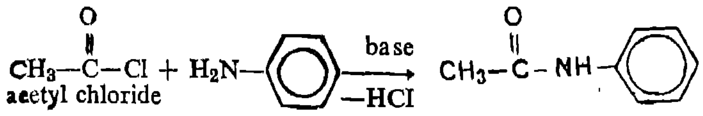
$$C_6H_5NH_2 + O{=}CH{-}C_6H_5 \longrightarrow \underset{\text{benzalaniline}}{C_6H_5N{=}CHC_6H_5} + H_2O$$

Schiff's bases can be reduced to secondary amines and therefore this method provides a convenient route to their preparation.

$$RN{=}CHR \xrightarrow{\text{reduction}} RNHCH_2R$$

(ii) *Reactions with acid chlorides and acid anhydrides*

Acid chlorides react vigorously with primary and secondary amines to give substituted acid amides. Aniline reacts with acetyl chloride to give acetanilide. The reaction is generally done in the presence of some base like pyridine or sodium hydroxide to neutralize the HCl formed



acetyl chloride

acetanilide or N-methyl ethanamide

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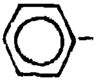
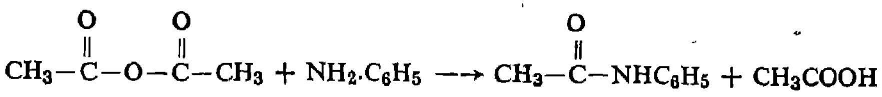
*  —CH= group is called the benzal group.

Substituted acid amides like acetanilide could also be considered as acyl derivatives of amines In the above case acetanilide is acetyl derivative of aniline. Only the primary and the secondary amines undergo acylation reaction. Tertiary amines do not undergo acylation (even though they are bases) because they do not have hydrogen, attached to nitrogen which may be lost as HCl.

The reactions of amines with acid anhydrides also yield acyl derivatives of amines but this reaction is slower than the reaction with acyl chlorides

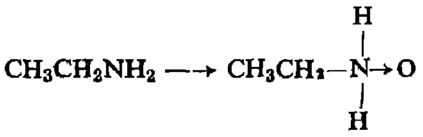


$$CH_3-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-CH_3 + NH_2.C_6H_5 \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-NHC_6H_5 + CH_3COOH$$

Acylation of a compound is the introduction of $R-\overset{\overset{O}{\|}}{C}-$ group into its molecule; the introduction of $CH_3-\overset{\overset{O}{\|}}{C}-$ group is called acetylation Acetylation can be carried out with acetyl chloride in the presence of a base or with acetic anhydride. Introdution of $C_6H_5-\overset{\overset{O}{\|}}{C}-$ group into a compound is called *benzoylation.* Benzoylation of an amine is done by reacting it with benzoyl chloride in presence of a base.

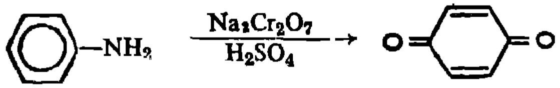
(e) *Oxidation of amines*

Amines undergo oxidation in air to form N-oxides which are the compounds having oxygen attached to nitrogen



$$CH_3CH_2NH_2 \longrightarrow CH_3CH_2-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{N}}\rightarrow O$$

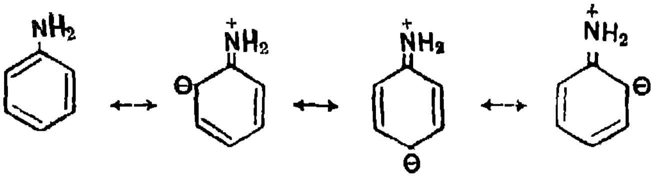
Especially aromatic amines get very easily oxidized on exposure to air leading to formation of complex coloured products. Pure amine can be recovered by distillation of a coloured sample When aniline is oxidized by strong oxidizing agents, some complex reactions take place Aniline gives a black dye on oxidation with sodium dichromate and sulphuric acid, this dye is called analine black. On controlled oxidation of aniline with the same reagents, *p*-benzoquinone is formed.



p-benzoquinone

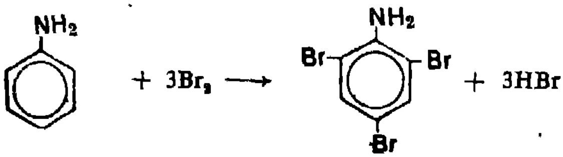
(f) *Ring substitution in aromatic amines*

We have seen that the amino group (more so —NHR or —NR$_2$ group) acts as a powerful activator and ortho-para director in aromatic electrophilic substitutions. These effects can be explained in terms of the electron delocalisation which increases electron density at the ortho and para positions.

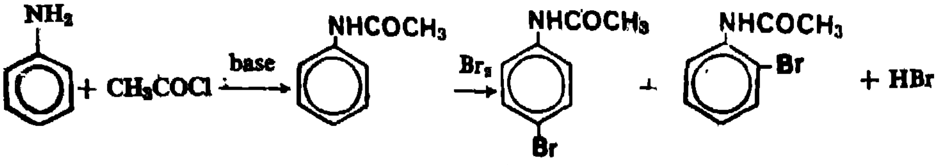


(i) *Halogenation*

Activation by amino group is so powerful that aniline gives 2, 4, 6-tribromoaniline with aqueous solution of bromine. Bromine enters the para and both the ortho positions

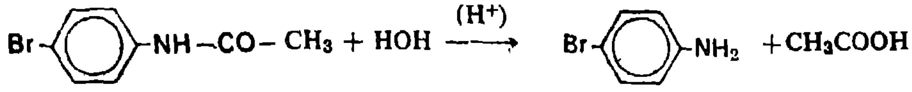


If a monobromo compound is desired, aniline is acetylated before bromination. The sequence of reactions can be,



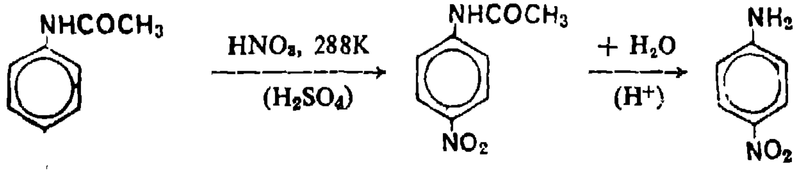
(major) (minor)

Electron withdrawal by carbonyl oxygen here makes nitrogen of the amide a poorer electron donor than that in the amine, though it still remains an activating and ortho-para directing group. From the *p*-bromoacetanilide, *p*-bromoaniline is obtained by acid-hydrolysis followed by addition of an alkali.



(ii) *Nitration*

Nitric acid is not only a nitrating agent but also a strong oxidizing agent, so direct use of HNO_3 leads to the formation of a lot of tarry oxidation products. Nitration of acetylated amine proceeds smoothly, the acetyl group can be removed after the nitration. This use of acetylation as an intermediate step is referred to as *protecting the amino group.*

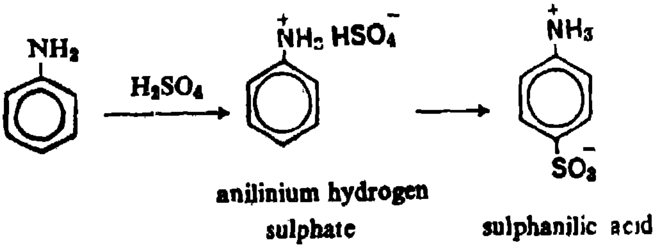


mainly

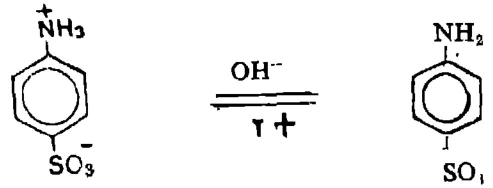
It would also be relevant to mention that in a strongly acidic solution, an amino group will undergo protonation. So substitution (nitration) reaction will be controlled by NH_3^+ group rather than $-NH_2$ group NH_3^+ is a deactivating and meta-directing group because of its positive charge So nitration under these conditions will give mostly the meta isomer

(iii) *Sulphonation*

Aniline is usually sulphonated by heating its salt, anilinium hydrogen sulphate, at 455–475 K. The chief product is *p*-amino benzene sulphonic acid. It is also called *sulphanilic acid.*



Sulphanilic acid is an important compound. It has a high melting point 553–573K; aniline melts at 267K and benzene sulphonic acid at 339K. Sulphanilic acid is insoluble in water and in organic solvents; aniline itself is soluble in organic solvents but not so much in water. Benzene sulphonic acid is extremely soluble in water. In fact, sulphonic acid group is introduced into substances to make them more soluble in water (e g., commercial detergents are very often sodium salts of alkyl benzene sulphonic acids, $RC_6H_4SO_3^-Na^+$) Amines are soluble in aqueous mineral acids because of their conversion to soluble salts, sulphanilic acid is soluble in aqueous bases; but insoluble in aqueous acids.

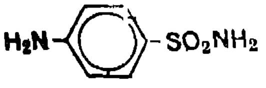


water insoluble
(I)

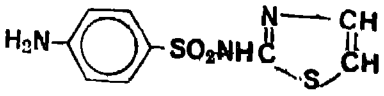
water soluble
(II)

So both as regards its melting point and solubility, sulphanilic acid is very different from aniline as well as benzene sulphonic acid. This strange behaviour of sulphanilic acid can be explained if we note that its molecule has the structure I shown above. It contains both $-\overset{+}{N}H_3$ and $-SO_3^-$ ionic groups in the same molecule. Sulphanilic acid is therefore a substance of a special kind. It is a dipolar ion or zwitter ion. This results from an acid and a base group being present in the same molecule. The high melting point and insolubility are characteristic of this internal salt formation. In an alkaline solution, the strongly basic OH^- ions remove the protons from $-\overset{+}{N}H_3$, and the resulting sodium salt of sulphanilic acid (II) is found to be soluble in water. However internal salt formation prevents its interaction with acids and thus sulphanilic acid does not dissolve in mineral acids or in water.

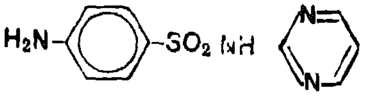
The amides of sulphonic acids are called sulphonamides. Some of these are widely used against bacterial infections. The sulphonamides are commonly called *sulpha drugs*. Out of a few hundred known sulpha drugs the formulae of three common ones are given below:



sulphanilamide
(from sulphanilic acid)



sulphathiazole



sulphadiazine

18.3-6 TEST OF AMINES

Amines are characterized through their basicity. A nitrogen containing compound that dissolves in cold dilute HCl is certainly an amine

Whether an amine is primary, secondary, or tertiary is best shown by Hinsberg Test. In this test the amine is shaken with benzene sulphonyl chloride in the presence of excess of aqueous potassium hydroxide A primary amine yields a clear solution from which on acidification an insoluble material separates. Secondary amine gives an insoluble compound which is unaffected by addition of an acid. A tertiary amine does not react, it remains insoluble in alkali, and can be dissolved in acid

$$\begin{tikzcd}
\underset{\substack{\text{primary}\\ \text{amine}}}{RNH_2+C_6H_5{-}SO_2Cl} \arrow[r, "OH^-"] & C_6H_5SO_2NHR^* \arrow[d, "KOH"] \\
\underset{\substack{\text{N-alkyl benzene sulphonamide}\\ \text{(insoluble)}}}{C_6H_5{-}SO_2NHR} & \underset{\text{(clear solution)}}{C_6H_5SO_2NR^-K^+} \arrow[l, "H^+"']
\end{tikzcd}$$

$$\underset{\substack{\text{secondary}\\ \text{amine}}}{R_2NH} + C_6H_5{-}SO_2Cl \xrightarrow{OH^-} \underset{\text{(insoluble)}}{C_6H_5SO_2NR_2^{**}} \xrightarrow[\text{or } H^+]{OH^-} \text{no reaction}$$

$$R_3N + C_6H_5{-}SO_2Cl \xrightarrow{OH^-} \text{no reaction}$$

Primary amines (both aliphatic and aromatic) can also be detected by heating with chloroform in the persence of an alkali. Isocyanides formed have an extremely unpleasant smell.

$$RNH_2 + CHCl_3 + 3KOH \longrightarrow \underset{\text{isocyanide}}{RNC} + 3KCl + 3H_2O$$

---

[*] N—alkyl benzene sulphonamide

[**] N, N dialkyl benzene sulphonamide

18.3-7 USES OF AMINES

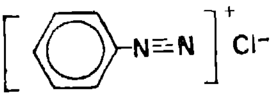
Aromatic amines are used extensively as intermediates for the commercial production of dyes, drugs, photographic developers and textiles. They also serve as starting materials for the synthesis of many compounds by the diazotization reaction. Amine salts of carboxylic acids have been used as herbicides.

18.4 DIAZONIUM SALTS

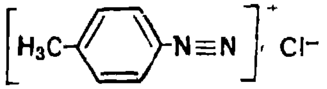
We have already seen that the reaction of primary aromatic amines with nitrous acid gives an important class of compounds called the diazonium salts. These salts have the general formula $ArN^+_2X^-$, where Ar is an aromatic ring and X is any anion like Cl^-, Br^-, HSO_4^-, etc. The diazonium salts have the structure :

$$[Ar{-}N \equiv N:]^+ X^-$$

They are named by adding the word dizonium the name of the parent aromatic compound to which they are related, followed by the name of the anion, e. g.



benzene diazonium chloride



p-toluene diazonium chloride

18.4-1 PREPARATION

The reaction between a primary aromatic amine and nitrous acid to produce diazonium salts is called *diazotization*. Since nitrous acid is itself unstable, it is generated in situ from sodium nitrite and a mineral acid like hydrochloric or sulphuric acid. The reaction is generally carried out at a low temperatures (273 to 278K) since the diazonium salts (and also nitrous acid) would decompose at higher temperatures. Diazotization of aniline can be represented as .

$$C_6H_5NH_2 + HONO + HCl \xrightarrow{273-278K} C_6H_5N_2^+Cl^- + 2H_2O$$

18.4-2 PHYSICAL PROPERTIES

Dry diazonium salts are crystalline solids. They are unstable and readily explode when in the dry state. So they are seldom isolated, and are used in the solutions in which they are prepared.

18.4-3 REACTIONS

Reactions of diazonium compounds can be classified into two categories (a) Replacement reactions (b) Coupling reactions.

Replacement reactions : Here the diazonium group on the ring is replaced by some other group. Nitrogen is lost in an elemental form

The following equations show how some of the replacement are carried out.

1. Hydrogen : $ArN_2X + H_3PO_2 + HOH \longrightarrow ArH + N_2 + H_3PO_3 + HX$

2. Hydroxyl : $ArN_2X + HOH \xrightarrow[(H^+)]{\text{warming}} ArOH + N_2 + HX$

3. Iodine : $ArN_2X + KI \longrightarrow ArI + N_2 + KX$

4. Chlorine : $ArN_2Cl \xrightarrow{Cu_2Cl_2,\ Cl^-} ArCl + N_2$

5. Bromine : $ArN_2Br \xrightarrow{Cu_2Br_2,\ Br^-} ArBr + N_2$

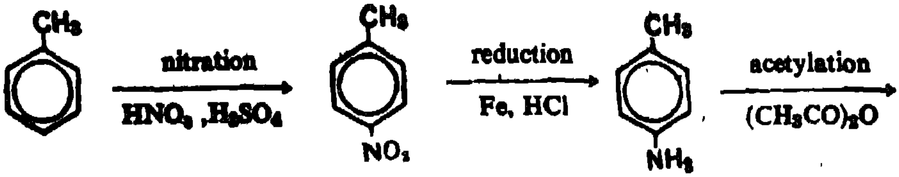
6. Cyanide group : $ArN_2X \xrightarrow{CuCN\ +\ CN^-} ArCN + N_2 + X^-$

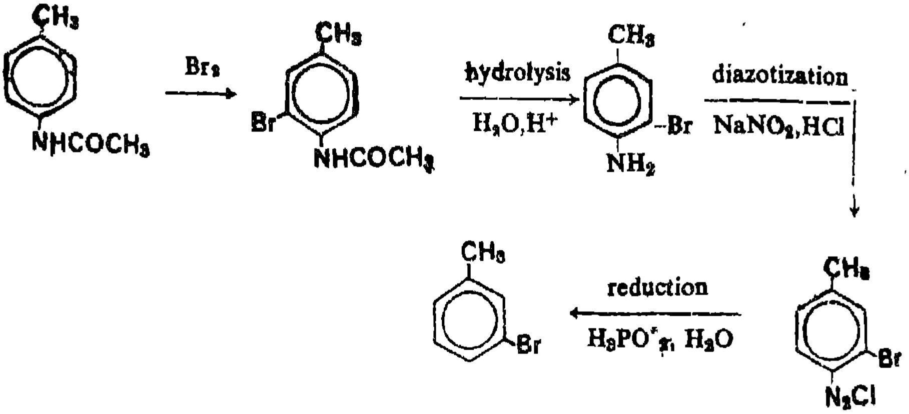
   Reactions 4, 5 and 6 are collectively known as Sandmeyer's reaction.

7. Gatterman reaction : $ArN_2X \xrightarrow[HX]{\text{Cu-powder}} ArX + N_2$

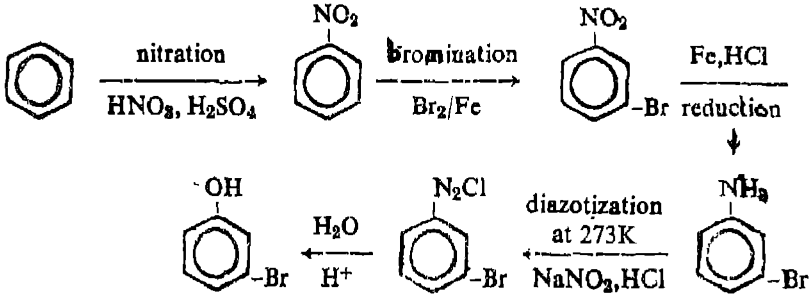
Gatterman's modification consists of using freshly prepared copper powder in the presence of corresponding hydrogen halides.

Since nitro group is easily introduced into an aromatic ring, the above sequence gives a method of introducing a variety of different functional groups into an aromatic molecule. Sometimes synthesis of a compound which can not be made directly is possible via the diazonium salt. For example, it is not possible to prepare *m*-bromotoluene directly either by bromination of toluene, or methylation of bromo benzene, both of which would give ortho/para isomers. The following sequence of reactions though long, gives the desired product :

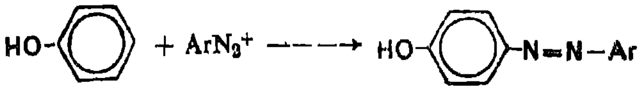




For *m*-bromophenol similarly, the diazonium compounds provide a possible route :



(b) Coupling Reactions : In these reactions nitrogen is retained in the product. Under proper conditions, diazonium salts react with aromatic compounds having strongly electron releasing groups like $-$ OH, $-$ NR$_2$, $-$ NHR, $-$ NH$_2$, etc. Substitution generally occurs at para to this activating group. Phenols couple in mildly alkaline medium, and amines in mildly acidic medium. The reaction is an example of aromatic electrophilic substitution, in which the diazonium ion, ArN_2^+, acts as the attacking electrophile.

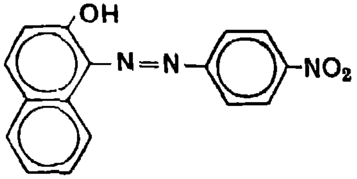


azo compound

---

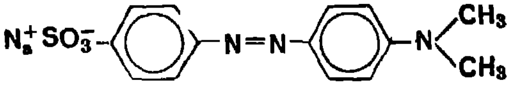
*Hypophosphorus acid.

The products are called azo compounds. They are strongly coloured. The colour can be yellow, orange, red, blue or even green depending on the structure of the compound. Azo compounds are of immense importance as dyes. About half the dyes used in industry today are azo dyes For example, para red, a dye has the formula ·



para red

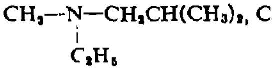
Some of the familiar acid—base indicators like methyl orange are also azo compounds.



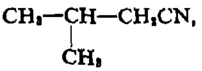
methyl orange

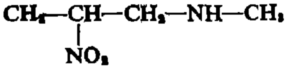
EXERCISES

18.1 Write the IUPAC names of the following compounds

p-$H_3COC_6H_4CN$,  $CH_3-\underset{C_2H_5}{\underset{|}{N}}-CH_2CH(CH_3)_2$, $C_6H_5NCH_2C_6H_5$,

p-$NO_2C_6H_4NH_2$, m-$CH_3C_6H_4NH(CH_3)_2$, $C_6H_5(CH_2)_2NH_2$,

$(CH_3CH_2CH_2)_4\overset{+}{N}\overset{-}{Br}$, p-$NO_2C_6H_4\overset{+}{N_2}\overset{-}{Cl}$  $CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2CN$,

 $CH_3-\underset{NO_2}{\underset{|}{CH}}-CH_2-NH-CH_3$

18.2 **Draw structures, name according to IUPAC and indicate primary, secondary and tertiary amine :**

(i) eight isomeric amines of formula $C_4H_{11}N$.

(ii) five isomeric amines of formula C_7H_9N that contain a benzene ring.

18.3 Illustrate the following terms :

Ambident nucleophile, *aci*-form, tautomerism, ammonolysis, quaternary ammonium salts, Gabriel synthesis, Hofmann bromamide method, nitrosation, exhaustive methylation, Hofmann elimination, Schiff base, acylation, benzoylation, zwitter ion, Hinsberg test, diazotisation, Sandmeyer reaction, Gattermann reaction, coupling reaction.

18.4 Account for the following :

(i) Alkane nitrites are higher boiling than the corresponding alkyl halides.

(ii) Tertiary nitroalkanes can not tautomerise to *aci*-form

(iii) It is difficult to prepare pure amines by ammonolysis of alkyl halides.

(iv) Amines are higher boiling compounds than hydrocarbons of corresponding molecular masses but have lower boiling points than the corresponding alcohols or carboxylic acids.

(v) Aniline is a weaker base than cyclohexyl amine.

(vi) $C_6H_5\overset{+}{N}(CH_3)_3\overset{-}{O}H$ is a stronger base than NH_4OH.

(vii) *p*-methoxy aniline is a stronger base than aniline and *p*-nitroaniline is a weaker base than aniline.

(viii) Methyl amine in water reacts with ferric chloride to precipitate ferric hydroxide.

(ix) Silver chloride dissolves in methyl amine solution.

(x) Tertiary amines do not undergo acylation.

(xi) Aniline is first converted into acetanilide than subjected to nitration with a mixture of sulphuric acid and nitric acid.

(xii) Sulphanilic acid is insoluble in water but soluble in aqueous base and aqueous mineral acids.

(xiii) Benzene sulphonyl chloride reacts with primary amine to give a product soluble in potassium hydroxide whereas the product of secondary amine and benzene sulphonyl chloride is insoluble in potassium hydroxide.

18.5 Fill up the blanks :

(i) $CH_3CH_2CH_2CONH_2 \xrightarrow[\text{heat}]{P_2O_5} ? \xrightarrow{H_2/Pt} ? \xrightarrow{HNO_2/HCl} ?$

(ii) $RNC \xrightarrow{H_2/Pt} ? \xrightarrow[\text{base}]{C_6H_5SO_2Cl} ?$

(iii) $RI \xrightarrow{NaCN} ? \xrightarrow{H_3O^+} ? \xrightarrow{NaOBr} ?$

(iv) $C_6H_5N(CH_3)_2 \xrightarrow{NHO_2} ?$

(v) $C_6H_5NH_2 \xrightarrow[\text{base}]{CH_3COCl} ? \xrightarrow{Br_2} ?$

(vi) $RCH_2NO_2 \xrightarrow{H_3O^+} ?$

(vii) $RNH_2 \xrightarrow{CHCl_3/KOH} ?$

(viii) $C_6H_5OH + C_6H_5\overset{+}{N}_2\overset{-}{Cl} \longrightarrow ?$

18.6 Accomplish the following conversions :

(i) Benzene → *m*-dichlorobenzene

(ii) *m*-nitroaniline → *m*-iodochlorobenzene

(iii) Toluene → *m*-bromotoluene

(iv) Benzene → *m*-bromophenol

(v) *p*-Nitroaniline → 1,2,3-tribromobenzene

18.7 (i) Write tests along with the chemical equations to distinguish compounds in each set :

(a) primary, secondary and tertiary nitro compounds,

(b) primary, secondary and tertiary amines.

(ii) How will you purify amines from non-basic impurities.

18.8 How does Hofmann elimination help in deciding the structures of unknown complex amines.

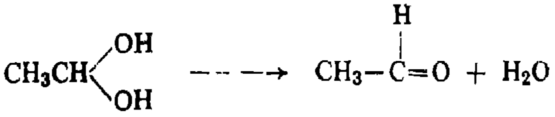
UNIT 19

Polyfunctional Compounds

So far we have studied the properties whose molecules have one functional group only. We have also seen that properties of functional groups may be somewhat modified by presence of other substituents in the molecules. In this unit we will study about some polyfunctional compounds in which more than one functional groups (similar or different) are present per molecule In these compounds sometimes the functional groups interact to such an extent as to produce certain properties which are characteristic of neither one group nor of the other, but of the particular combination of groups Here, we will lay emphasis on such special properties The functional groups are likely to influence each others behaviour more if they are closer together.

19.1 POLYHYDRIC ALCOHOLS

Polyhydric alcohols are compounds containing more than one alcoholic group. In these compounds each hydroxyl group is attached to a separate carbon atom. Two hydroxyl groups attached to the same carbon atom form an unstable arrangement which tends to lose a molecule of water spontaneously.



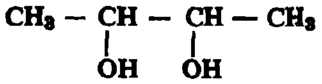
$$CH_3CH\langle^{OH}_{OH} \dashrightarrow CH_3-\overset{H}{\overset{|}{C}}=O + H_2O$$

In this section we will discuss two common polyhydroxy alcohols, namely ethylene glycol and glycerol.

19.1-1 ETHYLENE GLYCOL

Glycols are dihydroxy alcohols, the one with two hydroxyl groups attached to adjacent carbon atoms are called 1,2 glycols or *vic*-glycols. The glycols with OH groups on adjacent carbons atoms are most often named after the olefins from which they may be derived. When the two hydroxyl groups are attached to the extreme ends of a chain of carbon atoms, it is more convenient to call such glycols as polymethylene glycols.

Examples



$$CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3$$

2, 3-dihydroxybutane

$HO-CH_2-CH_2-CH_2-OH$

trimethylene glycol or 1, 3-dihydroxypropane.

$CH_3-CHOH-CH_2OH$

propylene glycol or 1, 2-dihydroxypropane

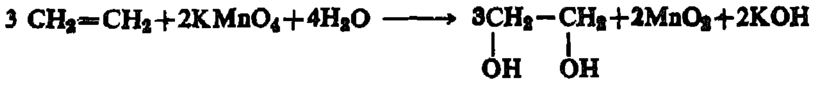
Ethylene glycol, commonly called glycol, has the structural formula CH_2OH-CH_2OH. It is a sweet syrupy liquid, heavier than water. Due to two sites for hydrogen bonding per molecule, glycol has a rather high boiling point, 470K, and is also highly soluble in water.

Due to its high solubility and low volatility, glycol (trade name Prestone) is preferred over methyl and ethyl alcohols as an antifreeze.[*]

Preparation

Glycol can be prepared from ethylene by any one of the following methods :

(i) Direct hydroxylation with Baeyer's reagent, cold dilute slightly alkaline $KMnO_4$.



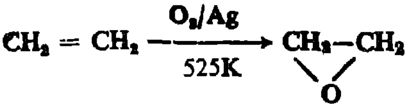
$$3\,CH_2=CH_2+2KMnO_4+4H_2O \longrightarrow 3\underset{\displaystyle OH}{\underset{|}{CH_2}}-\underset{\displaystyle OH}{\underset{|}{CH_2}}+2MnO_2+2KOH$$

---

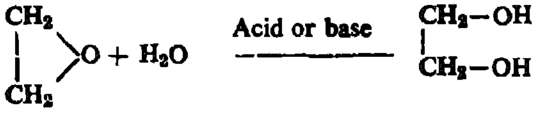
[*] The water in the car radiator is likely to freeze if the temperature falls below 273K. On freezing water expands, and this may cause the engine block to crack. Therefore it is necessary to add something to the water in the radiator to lower its freezing point. Such a substances is called an *antifreeze*. Alcohols are generally used as antifreeze because they are non-corrosive and are also miscible with water. Methyl and ethyl alcohols are sometimes used, but once the engine warms up, these alcohols evaporate easily and get boiled off (CH_3OH: b. p. 338K, C_2H_5OH : b.p. 351K). A mixture of 6 parts of water and 4 parts of glycol freezes at about 224K, 49 degrees below the freezing point of water.

(ii) **By hydrolysis of ethylene oxide :**

Ethylene epoxide or ethylene oxide can be prepared by catalytic oxidation of ethylene.



Ethylene oxide undergoes hydrolysis in the presence of an acid or a base to give glycol.

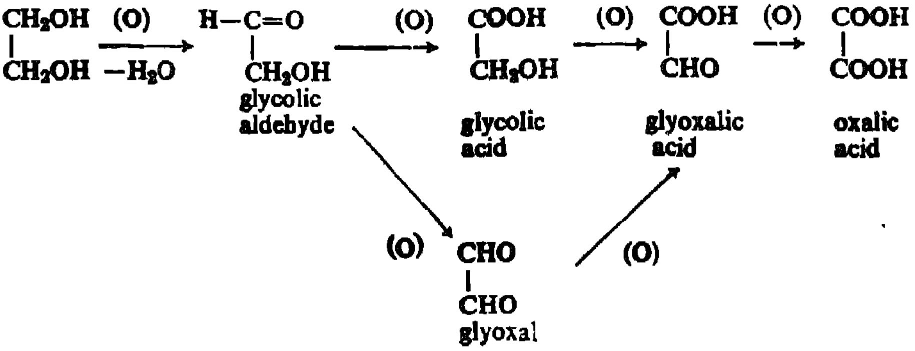


Reactions

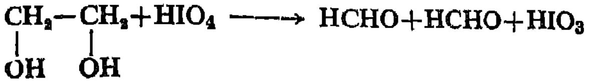
Glycol gives most of the reactions of primary alcohols like formation of ethers esters, etc. However, with two alcoholic groups there is a possibility of one or both hydroxyl groups reacting ; e.g. glycol may react with one or two equivalents of sodium to give mono or disodium derivative.

In addition glycol undergoes certain reactions which are characterstic of com ounds containing two hydroxyl groups on adjacent carbon atoms. Of these we will take the following two reactions :

(a) *Oxidation* : Ordinary oxidation of ethylene glycol gives a series of successive products. The final product usually is oxalic acid. The products formed in any one case depend on the conditions of oxidation such as the nature of oxidizing agent, temperature, etc.

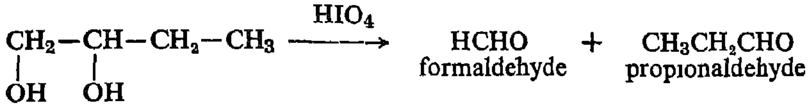


Oxidation with periodic acid proceeds differently. In this case *cleavage* of carbon-carbon bond takes place with the formation of two molecules of formaldehyde



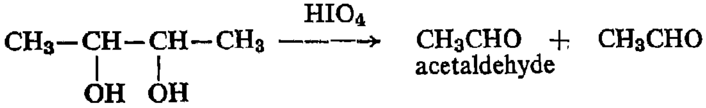
$$\underset{\mathrm{OH}}{\mathrm{CH_2}}-\underset{\mathrm{OH}}{\mathrm{CH_2}}+\mathrm{HIO_4} \longrightarrow \mathrm{HCHO+HCHO+HIO_3}$$

This reaction is particularly useful in structure determination of compounds containing hydroxyl groups on adjacent carbon atoms. The number of molecules of periodic acid that reacts with one molecule of a polyhydroxy compound gives the number of adjacent—OH group pairs. In addition the structures of aldehydes formed indicate the position of adjacent carbon atoms carrying the two—OH groups. Products obtained in periodic oxidation of isomeric butanediols would illustrate this :



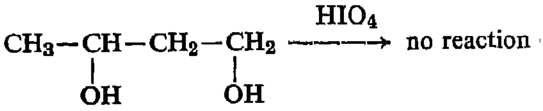
$$\underset{\mathrm{OH}}{\mathrm{CH_2}}-\underset{\mathrm{OH}}{\mathrm{CH}}-\mathrm{CH_2}-\mathrm{CH_3} \xrightarrow{\mathrm{HIO_4}} \underset{\text{formaldehyde}}{\mathrm{HCHO}} + \underset{\text{propionaldehyde}}{\mathrm{CH_3CH_2CHO}}$$

1, 2 butanediol



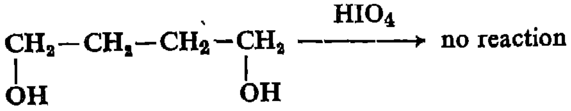
$$\mathrm{CH_3}-\underset{\mathrm{OH}}{\mathrm{CH}}-\underset{\mathrm{OH}}{\mathrm{CH}}-\mathrm{CH_3} \xrightarrow{\mathrm{HIO_4}} \underset{\text{acetaldehyde}}{\mathrm{CH_3CHO}} + \mathrm{CH_3CHO}$$

2, 3 butanediol



$$\mathrm{CH_3}-\underset{\mathrm{OH}}{\mathrm{CH}}-\mathrm{CH_2}-\underset{\mathrm{OH}}{\mathrm{CH_2}} \xrightarrow{\mathrm{HIO_4}} \text{no reaction}$$

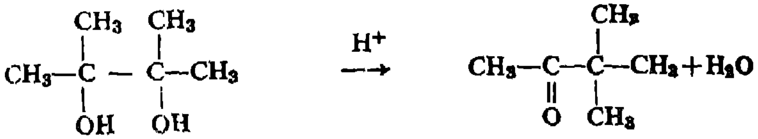
1, 3 butanediol



$$\underset{\mathrm{OH}}{\mathrm{CH_2}}-\mathrm{CH_2}-\mathrm{CH_2}-\underset{\mathrm{OH}}{\mathrm{CH_2}} \xrightarrow{\mathrm{HIO_4}} \text{no reaction}$$

1, 4 butanediol

(b) *Pinacol rearrangement* : Tetramethyl glycol, commonly called *pinacol*, undergoes an interesting reaction in the presence of a mineral acid. Dehydration takes place in such a way that rearrangement of carbon skeleton occurs giving a ketone called pinacolone



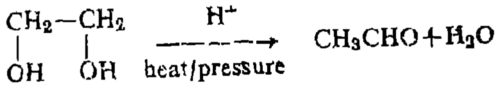
$$\underset{\underset{\text{OH}}{|}}{\overset{\overset{\text{CH}_3}{|}}{CH_3-C}}-\underset{\underset{\text{OH}}{|}}{\overset{\overset{\text{CH}_3}{|}}{C}}-CH_3 \xrightarrow{H^+} CH_3-\underset{\underset{\text{O}}{\|}}{C}-\underset{\underset{\text{CH}_3}{|}}{\overset{\overset{\text{CH}_3}{|}}{C}}-CH_3+H_2O$$

pinacol or
2, 3-dimethyl-2, 3-butanediol

pinacolone or
3, 3-dimethyl-2-butanone

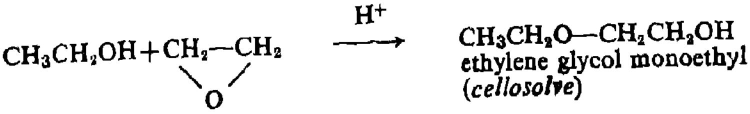
Such reactions in which an atom or group migrates to a new position in the molecule are called *rearrangement reactions*. The above reaction is called *pinacol–pinacolone rearrangement*.

Ethylene glycol itself gives acetaldehyde when treated with dilute sulphuric acid under pressure in a sealed tube (also rearrangement).



$$\underset{\underset{\text{OH}}{|}}{CH_2}-\underset{\underset{\text{OH}}{|}}{CH_2} \xrightarrow[\text{heat/pressure}]{H^+} CH_3CHO+H_2O$$

Ethers of glycol can be easily obtained by the reaction of ethylene oxide with an alcohol in the presence of a small amount of sulphuric acid. Some of these are important industrial solvents.



$CH_3CH_2OH+CH_2-CH_2$ (O) $\xrightarrow{H^+}$ $CH_3CH_2O-CH_2CH_2OH$
ethylene glycol monoethyl ether
(*cellosolve*)

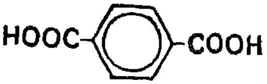
Cellosolve is a good solvent for cellulose nitrate which is extensively used in the manufacture of lacquers and enamels. Carbitol has two ether groups and an alcoholic group It is an excellent solvent for oils, waxes and resins. Diglyme is a useful laboratory solvent as a high boiling ether.

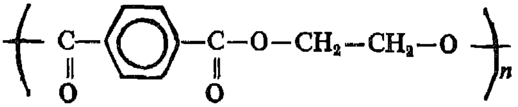
$$C_2H_5-OCH_2-CH_2-OCH_2-CH_2-OH$$

carbitol

$$CH_3-OCH_2-CH_2-O-CH_2-CH_2-OCH_3$$

diglyme

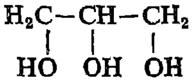
Some esters of glycol are industrially important. Dacron is a polyester of ethylene glycol formed with terephthalic acid,  . Dacron is extensively used for making synthetic fibers.



dacron

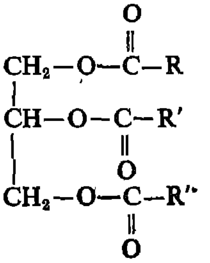
19.1-2 GLYCEROL

Glycerol (trade name glycerine) has the structure,



$$\underset{\text{HO}}{\text{H}_2\text{C}}-\underset{\text{OH}}{\text{CH}}-\underset{\text{OH}}{\text{CH}_2}$$

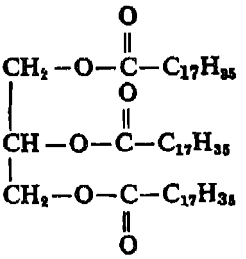
IUPAC name of this compound would be 1, 2, 3-propane-triol. Glycerol is an important industrial substance. Almost all fats are carboxylic esters of glycerol, they are therefore called glycerides, more specifically they should be called triacyl glycerols.



triacylglycerol or a glyceride in which R, R′, R″ may be the same or different alkyl groups.

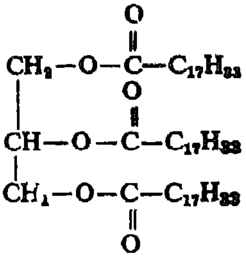
A glyceride molecule may have different acid residues. The proportions of various acids vary from fat to fat. Each fat has its characteristic composition which does not differ from sample to sample With only a few exceptions, the fatty acids are all straight chain compounds ranging from three to eighteen carbon atoms. Except for

C_3 and C_6 acids, acids containing only an even number of carbon atoms are present in fats in substantial amounts. Besides saturated acids, unsaturated acids containing one or more double bonds may also be present in a fat. Generally, fats with a high proportion of unsaturated fatty acids are liquids at ordinary temperatures and are called oils. Glyceryl tristearate for example melts at 344K whereas glyceryl trioleate (unsaturated) melts at 290K.



$$\begin{array}{l} CH_2-O-\overset{\overset{\displaystyle O}{\|}}{C}-C_{17}H_{35} \\ | \\ CH-O-\overset{\overset{\displaystyle O}{\|}}{C}-C_{17}H_{35} \\ | \\ CH_2-O-\underset{\underset{\displaystyle O}{\|}}{C}-C_{17}H_{35} \end{array}$$

glyceryl tristearate
m.p. 344K



$$\begin{array}{l} CH_2-O-\overset{\overset{\displaystyle O}{\|}}{C}-C_{17}H_{33} \\ | \\ CH-O-\overset{\overset{\displaystyle O}{\|}}{C}-C_{17}H_{33} \\ | \\ CH_2-O-\underset{\underset{\displaystyle O}{\|}}{C}-C_{17}H_{33} \end{array}$$

glyceryl trioleate
m.p. 290K

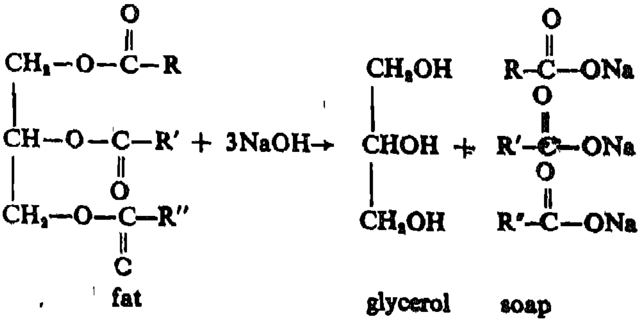
Fats make up one of the three major classes of food the other two being carbohydrates and proteins. They are also used as raw materials for many industrial processes like soap manufacture, preparation of long chain fatty acids and alcohols.

Physical properties of glycerol

Glycerol is a viscous, hygroscopic liquid denser than water. It has a sweet taste and is miscible with water or alcohol in all proportions. It has a high b.p. 563K. It is usually purified by distillation with superheated steam under reduced pressure.

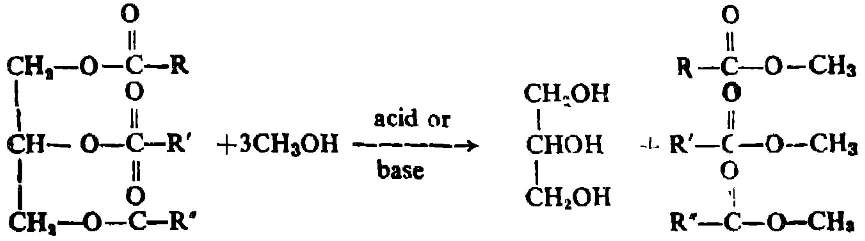
Preparation

Most of the glycerol is obtained as a by-product from soap manufacture. Saponification or hydrolysis of a fat with sodium hydroxide gives sodium salts of the long chain fatty acids, called soaps, and glycerol

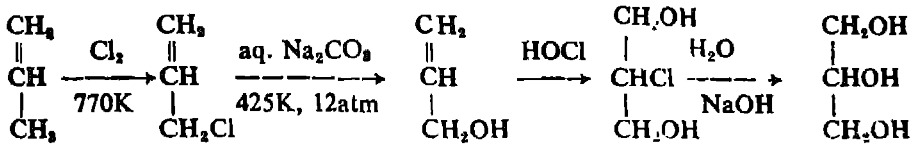


$$\begin{array}{l} CH_2-O-\overset{\overset{\displaystyle O}{\|}}{C}-R \\ | \\ CH-O-\underset{\underset{\displaystyle O}{\|}}{C}-R' \\ | \\ CH_2-O-\underset{\underset{\displaystyle C}{\|}}{C}-R'' \end{array} + 3NaOH \rightarrow \begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + \begin{array}{l} R-\overset{\overset{\displaystyle O}{\|}}{C}-ONa \\ R'-\overset{\overset{\displaystyle O}{\|}}{C}-ONa \\ R''-\overset{\overset{\displaystyle O}{\|}}{C}-ONa \end{array}$$

Glycerol can be liberated from fats by the transesterification reaction with methanol in presence of an acid or a base.



Another industrial source of glycerol is also hydration reaction of propylene (which is very cheaply obtained from cracking of petroleum products). Sequence of steps is as follows :

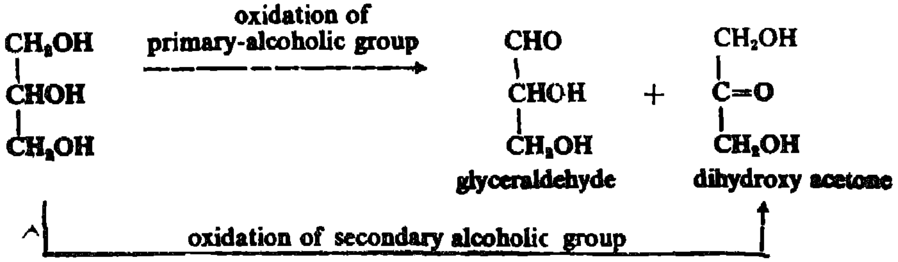


It should be noted that high temperature chlorination of propylene is a substitution reaction.

Reactions

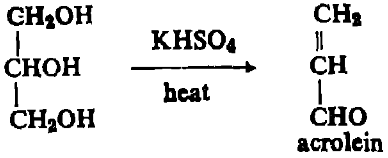
Glycerol has two primary and one secondary alcoholic groups It gives ethers, esters, etc., in the usual manner. Some of the important reactions of glycerol are discussed below :

(1) Oxidation : Mild oxidation with hydrogen peroxide in the presence of ferrous sulphate (Fenton's reagent) gives a mixture of glyceraldehyde and dihydroxy acetone.



Upon further oxidation both glyceraldehyde and dihydroxy acetone are oxidized into a mixture of formic, acetic and oxalic acids and finally CO_2

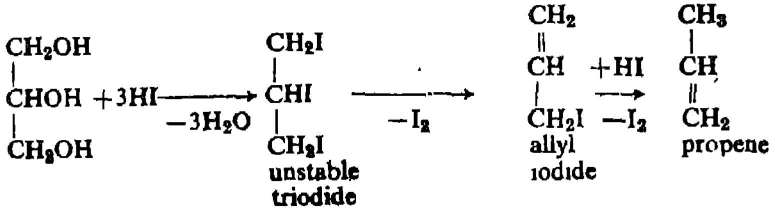
(2) *Dehydration*: When heated with potassium hydrogen sulphate, glycerol undergoes dehydration yielding an unsaturated aldehyde acrolein.



$$\begin{matrix} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{matrix} \xrightarrow[\text{heat}]{KHSO_4} \begin{matrix} CH_2 \\ \| \\ CH \\ | \\ CHO \\ \text{acrolein} \end{matrix}$$

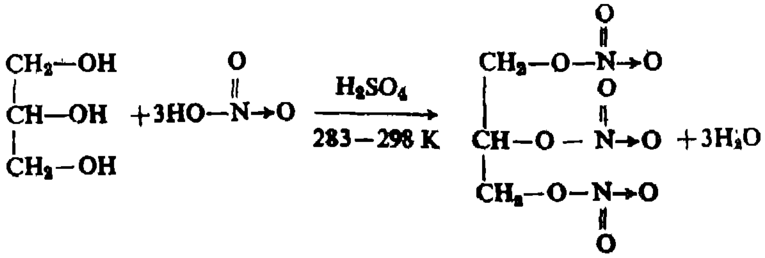
The pungent smell resulting from strong heating of fats is also due to formation of acrolein.

(3) *Reduction with hydriodic acid*: Hydriodic acid reduces glycerol to allyl iodide and finally to propene.



$$\begin{matrix} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{matrix} + 3HI \xrightarrow[-3H_2O]{} \begin{matrix} CH_2I \\ | \\ CHI \\ | \\ CH_2I \\ \text{unstable} \\ \text{triodide} \end{matrix} \xrightarrow[-I_2]{} \begin{matrix} CH_2 \\ \| \\ CH \\ | \\ CH_2I \\ \text{allyl} \\ \text{iodide} \end{matrix} + HI \xrightarrow[-I_2]{} \begin{matrix} CH_3 \\ | \\ CH \\ \| \\ CH_2 \\ \text{propene} \end{matrix}$$

(4) *Nitration*: Cautious addition of glycerol to a mixture of concentrated sulphuric and nitric acids, maintained at a temperature of 283–298 K, results in the formation of glyceryl trinitrate; an ester which has been traditionally called by the incorrect name 'nitroglycerine'.



$$\begin{matrix} CH_2-OH \\ | \\ CH-OH \\ | \\ CH_2-OH \end{matrix} + 3HO-\overset{\overset{O}{\|}}{N}\rightarrow O \xrightarrow[283-298\,K]{H_2SO_4} \begin{matrix} CH_2-O-\overset{\overset{O}{\|}}{N}\rightarrow O \\ | \\ CH-O-\overset{\overset{O}{\|}}{N}\rightarrow O \\ | \\ CH_2-O-\underset{\underset{O}{\|}}{N}\rightarrow O \end{matrix} + 3H_2O$$

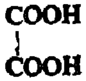
glyceryl trinitrate
(nitroglycerine)

Glyceryl trinitrate is a highly explosive substance. A mixture of glyceryl trinitrate and glycetyl dinitrate absorbed on kieselguhr (a kind of porous earth) is called *dynamite*. Dynamite was discovered by Alfred Nobel, well known for instituting Nobel Prizes. Explosives today are used not only for making bombs but also for rock blasting. Taken internally in medicinal doses, glyceryl trinitrate causes dilation of blood vessels and lowers blood pressure.

Uses

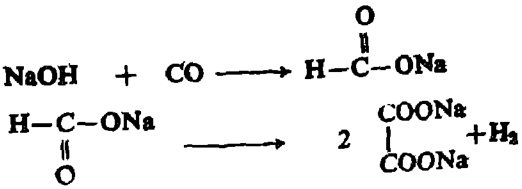
With a dicarboxylic acid like phthalic acid glycerol forms a cross-linked polyester called *glyptal* which is used as an alkyd resin. Apart from the manufacture of glyceryl trinitrate and glyptal, glycerol is used as a preservative and sweetening agent for foods. It is used in medicines like cough syrups, lotions, etc. It is also used in making cosmetics, in textile processing and as a softening agent for nitrocellulose. A covering of glycerol on fruit prevents their drying up in air as glycerine is sufficiently hygroscopic to absorb moisture from air.

19.2 OXALIC ACID



$$\begin{array}{c}COOH\\ |\\ COOH\end{array}$$

Oxalic acid is the first member of the dicarboxylic acid series. Its IUPAC name is ethanedioic acid. It is widely distributed in nature and occurs in rhubarb, wood sorrel, etc. Oxalic acid is one of the oldest organic acids known. Scheele prepared it in 1776 by oxidation of cane sugar with nitric acid. In 1829 Gay Lussac discovered that oxalic acid can be prepared by fusion of saw dust with sodium hydroxide. For many years this formed the commercial method for manufacture of oxalic acid These days oxalic acid is prepared by heating sodium formate, which is itself prepared by the reaction of carbon monoxide with sodium hydroxide under pressure. Hydrogen obtained as a by-product in this process is very pure.

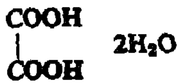


$$NaOH + CO \longrightarrow H-\overset{\overset{\displaystyle O}{\|}}{C}-ONa$$

$$H-\underset{\underset{\displaystyle O}{\|}}{C}-ONa \longrightarrow 2\begin{array}{c}COONa\\ |\\ COONa\end{array}+H_2$$

Physical Properties

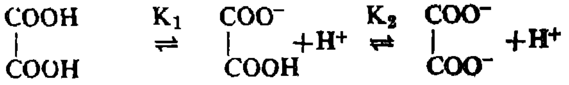
Oxalic acid crystallizes from water solutions as a dihydrate,



$$\begin{array}{c}COOH\\ |\\ COOH\end{array}2H_2O$$

It is sufficiently soluble in water and only slightly soluble in organic solvents.

Oxalic acid is a dibasic acid. As with other acids containing more than one ionisable hydrogen atoms per molecule (H_2SO_4 ,H_3PO_4), the ionisation of the second carboxyl group occurs less readily than ionisation of the first one. K_1 for oxalic acid is about a thousand times K_2 for it.



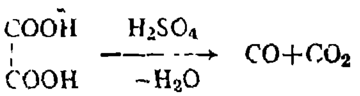
$$\begin{array}{l}COOH\\|\\COOH\end{array} \underset{}{\overset{K_1}{\rightleftharpoons}} \begin{array}{l}COO^-\\|\\COOH\end{array} + H^+ \overset{K_2}{\rightleftharpoons} \begin{array}{l}COO^-\\|\\COO^-\end{array} + H^+$$

$K_1 = 5.4 \times 10^{-2}$ $K_2 = 5.2 \times 10^{-5}$

This can be explained by the fact that more energy is required to separate a proton from the anion than from the uncharged oxalic acid molecule.

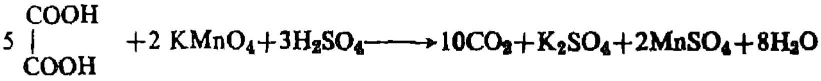
Reactions

Oxalic acid forms both normal and acid salts, esters and amides under the same conditions as for monocarboxylic acids. However, oxalic acid does not form any anhydride, dehydration of oxalic acid with concentrated sulphuric acid results in its decomposition into a mixture of CO and CO_2.



$$\begin{array}{l}COOH\\|\\COOH\end{array} \xrightarrow[-H_2O]{H_2SO_4} CO + CO_2$$

Oxalic acid is oxidized quantitatively by a hot acidified solution of potassium permanganate with sulphuric acid :



$$5\begin{array}{l}COOH\\|\\COOH\end{array} + 2\,KMnO_4 + 3H_2SO_4 \longrightarrow 10CO_2 + K_2SO_4 + 2MnSO_4 + 8H_2O$$

This reaction is used for standardisation of $KMnO_4$ solutions.*

Oxalic acid is extensively used as a mordant in dyeing and printing. Some of the higher homologues of oxalic acid are also important. Malonic acid COOH–CH_2 COOH and its esters are important intermediates in organic synthesis. Adipic acid gives the familiar Nylon 66, a polyamide on reaction with hexamethylene diamine

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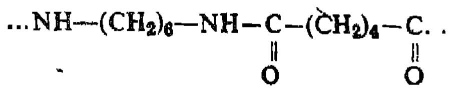
* In this respect oxalic acid differs from acetic acid which is stable both to heat as well as action of oxidizing agents.

$$\underset{\text{adipic acid}}{HOOC(CH_2)_4.COOH} + \underset{\text{hexamethylene diamine}}{NH_2-(CH_2)_6NH_2} \longrightarrow$$



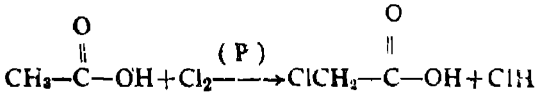
$$...NH-(CH_2)_6-NH-\underset{\underset{O}{\|}}{C}-(CH_2)_4-\underset{\underset{O}{\|}}{C}..$$

Nylon 66

Like dacron, nylon is also an important synthetic material for making fibres for cloth

19.3 CHLOROACETIC ACID ($ClCH_2-COOH$)

Chloroacetic acid is prepared by the chlorination of glacial acetic acid according to the Hell-Volhard-Zelinsky reaction (Section 17.4-5).



$$CH_3-\overset{\overset{O}{\|}}{C}-OH+Cl_2\xrightarrow{(P)}ClCH_2-\overset{\overset{O}{\|}}{C}-OH+ClH$$

Chloroacetic acid is a white solid, m. p. 334K, b. p. 463K It is very soluble in water and has an appreciably higher degree of ionization compared to acetic acid.

Chloroacetic acid has two reactive centres.

(i)—COOH (ii) C—Cl bond

(i) Carboxyl group shows its usual reactivity forming salts, esters and acid chloride in the usual manner

(ii) Chlorine here reacts in the same way as in alkyl halides; the chlorine atom may be replaced by cyano, hydroxy, ethoxy, amino and other groups, by the usual replacement reactions of alkylhalides. Chloroacetic acid is used in the manufacture of indigo

19.4 GLYCINE (NH_2CH_2COOH)

Glycine or aminoacetic acid (NH_2CH_2COOH) is the first member of the amino acids series. These compounds have amino as well as carboxyl groups.

Amino acids are the building blocks for proteins (see Unit—20) Glycine was obtained by Braconnet in 1820 by the hydrolysis of gelatin (which contains 25% glycine).

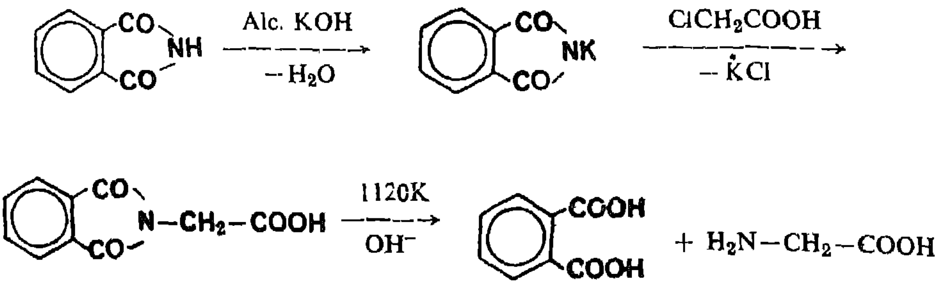
Glycine can be prepared from chloroacetic acid by its reaction. with ammonia Chloroacetic acid is shaken with excess of ammonia to get a good yield of glycine, but then it becomes difficult to separate glycine from ammonium chloride, solubilities of ammonium chloride and the amino acid are very similar One method of purification consists of adding freshly precipitated cupric hydroxide to the impure material, expelling ammonia by boiling, separating the sparingly soluble cupric aminoacetate from $CuCl_2$ by fractional crystallization Copper is then precipitated as sulphide with H_2S and glycine crystallized from the remaining solution

$$ClCH_2COOH + 3NH_3 \longrightarrow NH_2CH_2COONH_4 + NH_4Cl$$

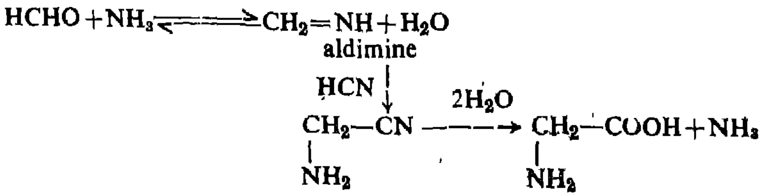
$$\Big\downarrow \text{Add } Cu(OH)_2 \text{ and boil to expel } NH_3$$

$$\underset{\text{glycine}}{NH_2CH_2COOH} \xleftarrow[-CuS]{+H_2S} \underset{\text{(separated from } CuCl_2 \text{ by crystallization)}}{(NH_2CH_2COO)_2Cu}$$

Gabriels phthalimide method gives another way of converting chloroacetic acid into glycine. This method has the advantage that no side products are formed and purification is easy



Strecker devised a convenient method for the synthesis of glycine starting from formaldehyde



$$HCHO + NH_3 \rightleftharpoons \underset{\text{aldimine}}{CH_2{=}NH} + H_2O$$

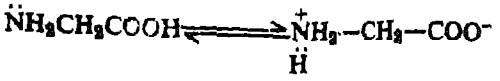
$$\Big\downarrow HCN$$

$$\underset{NH_2}{\underset{|}{CH_2}}-CN \xrightarrow{2H_2O} \underset{NH_2}{\underset{|}{CH_2}}-COOH + NH_3$$

The first two reactions can be done in one operation by treating the aldehyde with a mixture of NH_4Cl and KCN. The aldimine first formed reacts rapidly with HCN, forming aminonitrile, which can then be hydrolyzed to glycine.

Reactions

Glycine contains two reactive groups, the amino and the carboxyl, each of which so modifies the character of the other, that glycine can not be considered merely as an amine or an acid. The carboxyl group has the ability to lose a proton, whereas amino group may accept a proton, the molecule, therefore, exists largely as an internal salt known as zwitter ion ;



$$\ddot{N}H_2CH_2COOH \rightleftharpoons \overset{+}{N}H_2{-}CH_2{-}COO^-\ (\text{with } \ddot{H} \text{ below } N)$$

(compare sulphanilic acid)

The high dipole moment and high melting point (above 573K) of glycine indicate the salt like structure of this substance. It has a very low solubility in organic solvents like alcohol, but is freely soluble in water.

The acidity and basicity constants for glycine are quite low; $K_a=1.6\times10^{-10}$ and $K_b=2.5\times10^{-12}$. These values are consistent with its zwitter ion character, i e. the acid centre is an ammonium ion rather than a free carboxyl group and the basic centre is a carboxylate ion rather than a free amino group.

Isoelectric Point : The zwitter ion of glycine is amphoteric, it may either lose or gain a proton. In water solutions glycine tends to lose a proton, hence the negative amino acid ion migrates to the anode when the solution is electrolyzed.

$$\overset{+}{N}H_3CH_2COO^- + H_2O \rightleftharpoons \underset{\text{migrates to anode}}{NH_2CH_2COO^-} + H_3O^+$$

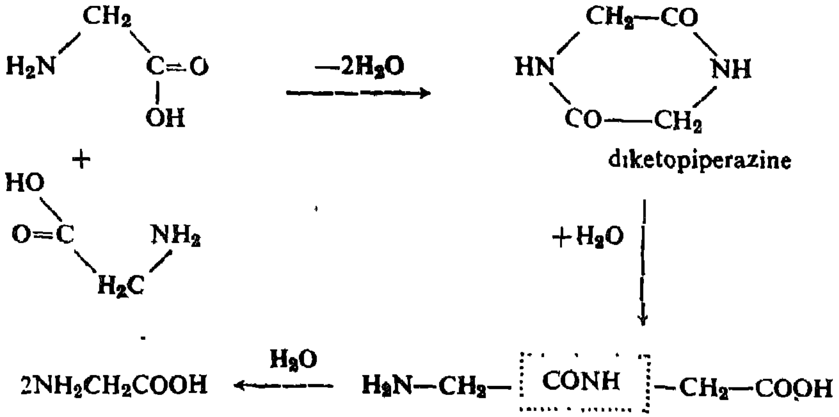
The addition of an acid converts the zwitter ion to a cation, which migrates to cathode during electrolysis.

$$NH_2{-}CH_2{-}COOH + H^+ \longrightarrow \underset{\text{migrates to cathode}}{\overset{+}{N}H_3CH_2{-}COOH}$$

So glycine forms an anion or a cation depending on the hydrogen ion concentration of the solution. At pH 6, glycine has an equal tendency to form either of these forms; hence the net charge of the zwitter ion is zero at a pH of 6. This pH value is called the iso-electric point of glycine. Other amino acids also have characteristic isoelectric points.

Internal diamide formation

When glycine is heated, it loses water to give a cyclic diamide, called diketopiperazine.

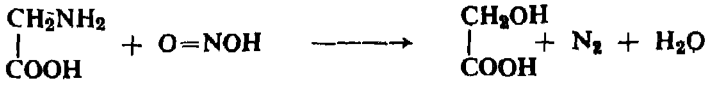


As shown partial hydrolysis of diketopiperizine gives an amide formed from two molecules of glycine. This is a dipeptide of glycine. In addition to the above reactions which may be considered to be due to interaction of amino and carboxyl groups, glycine gives some reactions typical of amino group and some of carboxyl group.

(a) Reactions of amino group

Glycine gives most of the reactions of primary amino group :

(i) *Liberation of nitrogen with nitrous acid :* Van Slykes method for estimation of amino acids is based on this reaction.



$$\begin{matrix} CH_2NH_2 \\ | \\ COOH \end{matrix} + O=NOH \longrightarrow \begin{matrix} CH_2OH \\ | \\ COOH \end{matrix} + N_2 + H_2O$$

1 mole **1 mole**

(ii) *Acylation* : Glycine can be acetylated by treating it with acetic anhydride or acetyl chloride.

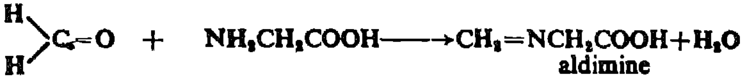
$$(CH_3CO)_2O + NH_2CH_2COOH \longrightarrow \underset{\text{acetyl glycine}}{CH_3CONHCH_2COOH} + CH_3COOH$$

Benzoylation can be done with benzoyl chloride. Benzoyl glycine is called *hippuric acid.* It is present in the urine of all vertebrates and in considerable amounts in the urine of horse.

$$C_6H_5COCl + NH_2CH_2COOH \longrightarrow \underset{\text{benzoyl glycine or hippuric acid}}{C_6H_5-CONHCH_2-COOH}$$

In the acyl derivatives of glycine, the amino group is converted to an amide, with consequent loss of basicity; so these compounds become quite acidic in nature due to increased freedom of the—COOH group.

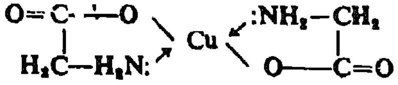
(iii) *Sorenson's formol titration* : This takes advantage of the reaction between formaldehyde and the amino group. In the aldimine thus formed, the amino group is blocked, and the free carboxyl group can be titrated with alkali using phenolphthalein as indicator.



$$\begin{matrix}H\\ H\end{matrix}\!\!>C=O + NH_2CH_2COOH \longrightarrow \underset{\text{aldimine}}{CH_2=NCH_2COOH} + H_2O$$

(b) Reactions of the Carboxyl Group

(i) *Salt formation :* Glycine forms salts in the usual manner. Copper salts have the deep blue colour of copper-ammonia complexes because of coordination with the amino group.



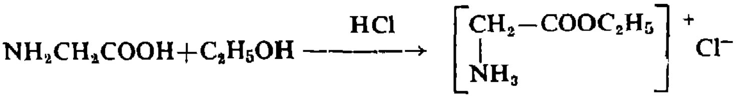
deep blue

(ii) *Decarboxylation :* When heated with barium hydroxide solution, glycine undergoes decarboxylation.

$$NH_2CH_2COOH + Ba(OH)_2 \longrightarrow CH_3NH_2 + BaCO_3 + H_2O$$

Similar decarboxylation is brought about by heating glycine in an inert solvent Putrefying bacteria also brings about decarboxylation of amino acids present in proteins. Bad smell associated with rotting proteins is due to the formation of amines by decarboxylation of amino acids.

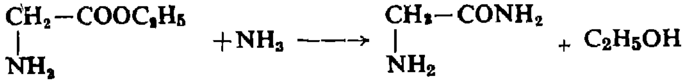
(iii) Glycine forms esters with alcohols. The ester formation blocks the carboxyl group and so the esters of glycine are distinctly basic in nature In fact when glycine is esterified with alcohol in the presence of HCl, ester hydrochloride is formed. Free ester can be liberated by addition of a mild base such as silver hydroxide.



$$NH_2CH_2COOH + C_2H_5OH \xrightarrow{HCl} \left[\begin{array}{l} CH_2-COOC_2H_5 \\ | \\ NH_3 \end{array}\right]^+ Cl^-$$

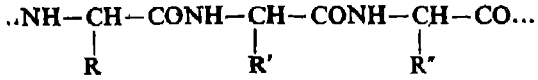
glycine ethyl ester hydrochloride

(iv) Glycine amide is formed by reacting glycine ester with ammonia.



$$\begin{array}{l} CH_2-COOC_2H_5 \\ | \\ NH_2 \end{array} + NH_3 \longrightarrow \begin{array}{l} CH_2-CONH_2 \\ | \\ NH_2 \end{array} + C_2H_5OH$$

Peptides are chain-like intermolecular amides of amino acids. In these, the carboxyl group of one amino acid molecule reacts and links with the amino group of a neighbouring molecule and so on. Peptides of relatively low molecular masses are called polypeptides; higher molecular mass materials are proteins. Molecular masses of proteins range from 15,000 to 20,000,000. Enzymes and some of the hormones like insulin are proteins in nature (see Unit 20).



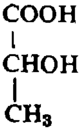
$$..NH-\underset{\displaystyle R}{\underset{|}{CH}}-CONH-\underset{\displaystyle R'}{\underset{|}{CH}}-CONH-\underset{\displaystyle R''}{\underset{|}{CH}}-CO...$$

a peptide

19.5 HYDROXY ACIDS

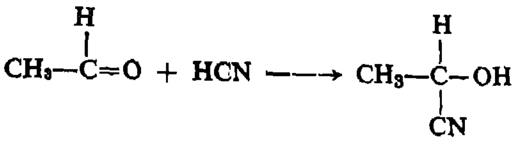
Lactic, tartaric and citric acids are aliphatic hydroxy acids, and salicylic acid is an aromatic hydroxy acid. They all have one or more hydroxyl groups and a carboxyl group.

19.5.1 LACTIC ACID



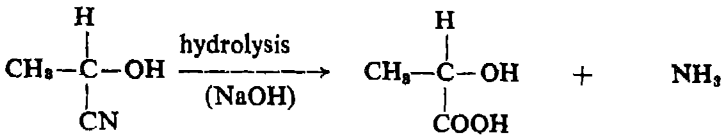
$$\begin{array}{l} COOH \\ | \\ CHOH \\ | \\ CH_3 \end{array}$$

Lactic acid is 2-hydroxypropanoic acid. It occurs in sour milk. Curdling of milk is due to the bacterial fermentation of milk sugar, lactose to lactic acid. Commercially, it is produced by fermentation of sugar solutions with *lactic acid* *bacillus*. Synthetically, it can be prepared from acetaldehyde through cyanohydrin formation.



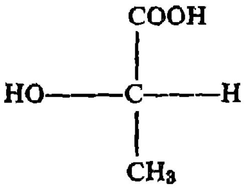
$$CH_3-\overset{\overset{\Large H}{|}}{C}=O + HCN \longrightarrow CH_3-\underset{\underset{\Large CN}{|}}{\overset{\overset{\Large H}{|}}{C}}-OH$$

cyanohydrin of acetaldehyde



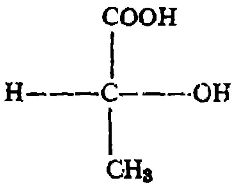
$$CH_3-\underset{\underset{\Large CN}{|}}{\overset{\overset{\Large H}{|}}{C}}-OH \xrightarrow[(NaOH)]{\text{hydrolysis}} CH_3-\underset{\underset{\Large COOH}{|}}{\overset{\overset{\Large H}{|}}{C}}-OH + NH_3$$

Lactic acid has an asymmetric carbon atom, therefore, it can have two optically active enantiomers shown below (see Unit 16).



$$HO-\underset{\underset{\Large CH_3}{|}}{\overset{\overset{\Large COOH}{|}}{C}}-H$$

d—lactic acid



$$H-\underset{\underset{\Large CH_3}{|}}{\overset{\overset{\Large COOH}{|}}{C}}-OH$$

l—lactic acid

Lactic acid obtained by synthesis and also by fermentation is racemic lactic acid. It can be separated (resolved) into dextro and laevo enantiomers under suitable conditions. Dextro rotatory enantiomer was isolated from an extract of muscle tissue by Berzelius (1808) and is called *sarco-lactic acid* (sarcos means flesh). In the muscle, lactic acid is supposed to form from the break down of glycogen, a polymeric form of glucose. *dl*-lactic acid is a hygroscopic, viscous, syrupy liquid, m. p 291 K. It is soluble in water, alcohol and ether. It is a much stronger acid than acetic acid, K_a-13.8 × 10^{-5} The OH group on α– carbon tends to withdraw electrons and makes release of proton from the — COOH group easier.

Reactions

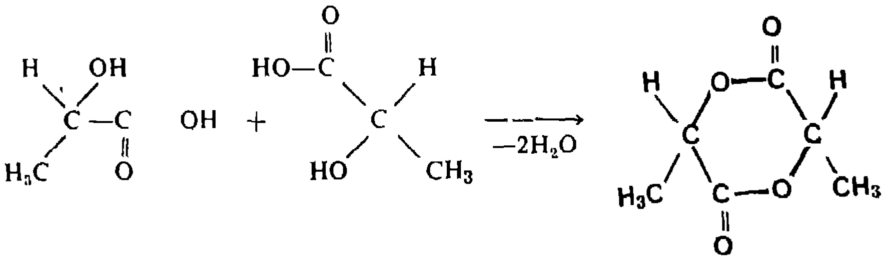
Lactic acid shows the usual properties of alcohols and acids. It forms salts, esters, and amides at the carboxyl group and undergoes acylation and oxidation at the alcoholic group. Both the groups react with PCl_3.

$$3CH_3CHOHCOOH + 2PCl_3 \longrightarrow 3CH_3CHClCOCl + 2H_3PO_3$$

When lactic acid is heated with dilute H_2SO_4, it decomposes into acetaldehyde and formic acid

$$CH_3CHOHCOOH \longrightarrow CH_3CHO + HCOOH$$

On being heated alone, it forms a cyclic diester known as *lactide* A small amount of acid also decomposes to acetaldehyde, $CO + H_2O$.

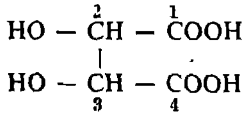


lactide

(also $CO + H_2O + CH_3CHO$)

Lactic acid is used as an acidulant in food stuffs In medicine, calcium lactate is used for calcium deficiency Antimony lactate is used in dyeing wool and in calico printing Ethyl lactate is used as a solvent for nitrocellulose in lacquer industry Lactic acid is also used for removing lime from hides before tanning

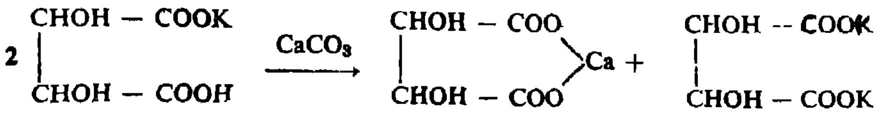
19 5-2 TARTARIC ACID



$$\begin{array}{c} HO - \overset{2}{C}H - \overset{1}{C}OOH \\ | \\ HO - \underset{3}{C}H - \underset{4}{C}OOH \end{array}$$

Tartaric acid is 2,3—dihydroxy butane—1, 4—dioic acid. It is present **in grapes, tamarind and in some other sour fruits.** Tartaric acid is also formed during the **fermentation of grape juice. Scheele (1769) first isolated it from potassium hydrogen** tartrate, tartar or argol, which separates out in liquor fermentation tanks. This still forms the main commercial source of tartaric acid

Tartar is neutralized with calcium carbonate to convert it into sparingly soluble calcium **tartarate and** soluble potassium tartarate Potassium tartarate is also converted to calcium tartarate by adding $CaCl_2$. Addition of a calculated amount of sulphuric acid gives free tartaric acid, precipitating out calcium sulphate.

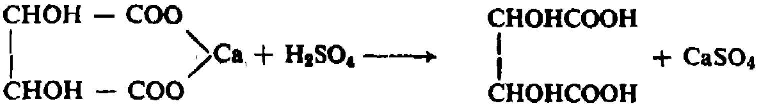


$$2\begin{array}{l}CHOH-COOK\\|\\CHOH-COOH\end{array}\xrightarrow{CaCO_3}\begin{array}{l}CHOH-COO\\|\\CHOH-COO\end{array}\!\!>Ca+\begin{array}{l}CHOH-COOK\\|\\CHOH-COOK\end{array}$$

potassium hydrogen tartrate

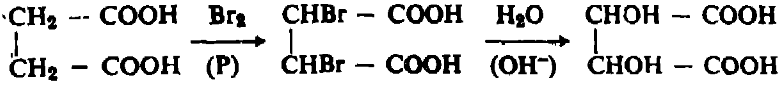
calcium tartarate (sparingly soluble)

potassium tartarate (soluble)



$$\begin{array}{l}CHOH-COO\\|\\CHOH-COO\end{array}\!\!>Ca+H_2SO_4\longrightarrow\begin{array}{l}CHOHCOOH\\|\\CHOHCOOH\end{array}+CaSO_4$$

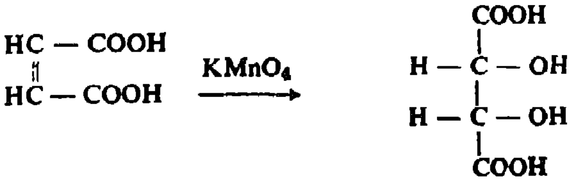
Synthetically, tartaric acid may be obtained by bromination of succinic acid (1, 4—butanedioic acid) and hydrolysis of the dibromosuccinic acid with alkali



$$\begin{array}{l}CH_2-COOH\\|\\CH_2-COOH\end{array}\xrightarrow[(P)]{Br_2}\begin{array}{l}CHBr-COOH\\|\\CHBr-COOH\end{array}\xrightarrow[(OH^-)]{H_2O}\begin{array}{l}CHOH-COOH\\|\\CHOH-COOH\end{array}$$

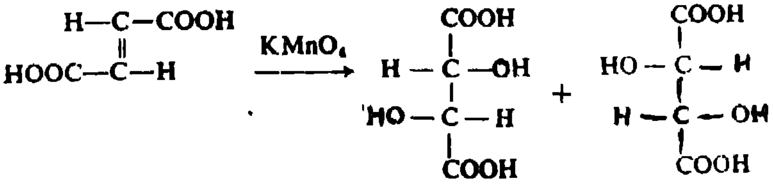
a mixture of *meso* and *racemic* tartaric acids

Unsaturated butene-dioic acids, the two geometrical isomers maleic and fumaric acids, also give tartaric acid on hydroxylation with potassium permanganate (cold, dilute, slightly alkaline) Maleic, the *cis*—isomer gives *meso*—tartaric acid, fumaric, the *trans*—isomer gives racemic tartaric acid.



$$\begin{array}{l}HC-COOH\\\|\\HC-COOH\end{array}\xrightarrow{KMnO_4}\begin{array}{c}COOH\\|\\H-C-OH\\|\\H-C-OH\\|\\COOH\end{array}$$

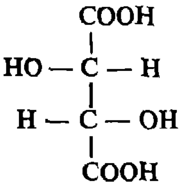
meso tartaric acid



$$\begin{array}{l}H-C-COOH\\\|\\HOOC-C-H\end{array}\xrightarrow{KMnO_4}\begin{array}{c}COOH\\|\\H-C-OH\\|\\HO-C-H\\|\\COOH\end{array}+\begin{array}{c}COOH\\|\\HO-C-H\\|\\H-C-OH\\|\\COOH\end{array}$$

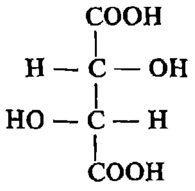
racemic tartaric acid

Tartaric acid has two similar asymmetric carbon atoms and therefore should have one pair of enantiomers and a meso form. These stereo-isomers of tartaric acid are shown below.



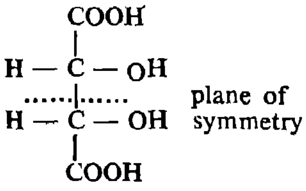
d-tartaric acid

I



l-tartaric acid

II



meso-tartaric acid

III

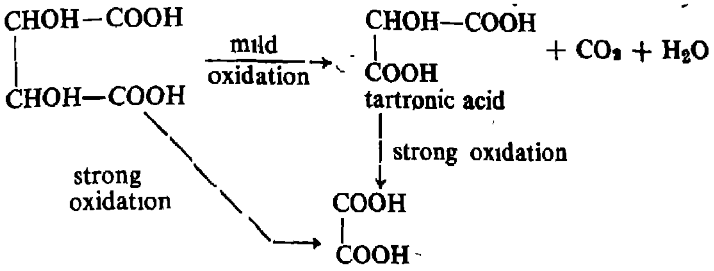
As seen before an equal amount of d-and l-tartaric acids mixed together gives racemic tartaric acid. Both racemic and *meso* tartaric acid are optically inactive but whereas racemic tartaric acid can be separated (resolved) into the d-and l-enantiomers under suitable conditions, *meso*-tartaric acid is unresolvable. *Meso*-tartaric acid is an example of *diastereo-isomerism.*

Stereoisomerism of tartaric acid has played an important role in the development of early ideas about optical isomerism. While examining crystals of sodium ammonium tartarate through a magnifying glass, Pasteur (1848) discovered that there were two types of crystals, some had hemihedral faces on the right and some on the left. He separated these crystals by careful hand picking, and isolated free tartaric acids from them.

Pasteur found that one type of these crystals yielded dextro-rotatory tartaric acid, and the other type laevo-rotatory tartaric acid. A mixture of the two in equal amounts was found to be optically inactive and was called racemic tartaric acid.

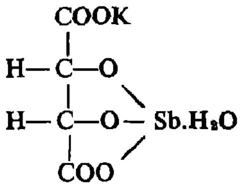
It was shown that tartaric acid obtained from grapes and that obtained by fermentation was dextro-rotatory and identical in every way with the dextro-isomer isolated by Pasteur.

Synthesis, as is expected, yields either a racemic or a *meso*-tartaric acid. All isomers of tartaric acid are stronger acids than acetic acid. On heating above 445K, tartaric acid decomposes with charring. Tartaric acid gets easily oxidized, mild oxidizing agents give tartronic acid, strong oxidizing agents break it into oxalic acid.



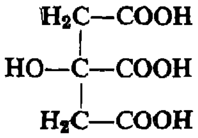
Tartaric acid reduces ammoniacal silver nitrate, so it is used in mirroring glass. Some of the salts of tartaric acid are important Cream of tartar, potassium hydrogen tartrate is a constituent of baking powders (mixtures of $NaHCO_3$ + $KH.C_4H_4O_6$, when warmed in moist dough, CO_2 is liberated which acts as a leavening agent).

Rochelle's salt is sodium potassium tartrate. Tartar emetic is a compound used as mordant in dyeing and as an emetic in medicine It is quite poisonous.



tartar emetic

19.5-3 CITRIC ACID



$$\begin{array}{l} H_2C-COOH \\ \quad\;| \\ HO-C-COOH \\ \quad\;| \\ H_2C-COOH \end{array}$$

Citric acid is a monohydroxy tricarboxylic acid. It is a crystalline solid containing one molecule of water. It occurs in many fruits, especially in citrus fruits like lemons and oranges. Lemon juice contains about 6-8% of citric acid, and forms one of the chief commercial sources of citric acid.

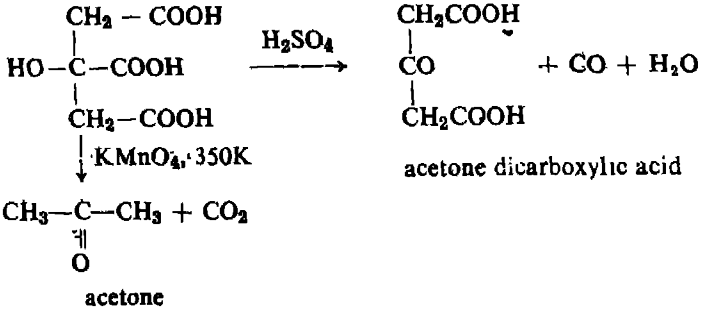
The juice is boiled to coagulate proteins, and filtered. The clear juice is neutralized with lime. Contrary to the behaviour of most salts, calcium citrate is less soluble in hot water than in cold, and it separates out from the hot solution.

Addition of a calculated quantity of sulphuric acid to calcium citrate gives free citric acid, precipitating out. $CaSO_4$

Citric acid is a white, crystalline solid containing one molecule of water of crystallisation. It is readily soluble in water and alcohol, but insoluble in ether

Reactions

Citric acid liberates CO on heating with conc sulphuric acid, but it does not char.



$$HO-C(CH_2COOH)_2-COOH \xrightarrow{H_2SO_4} CO(CH_2COOH)_2 + CO + H_2O$$

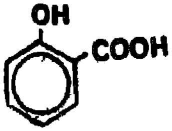
acetone dicarboxylic acid

$$HO-C(CH_2COOH)_2-COOH \xrightarrow{KMnO_4,\ 350K} CH_3-CO-CH_3 + CO_2$$

acetone

Hot $KMnO_4$ solution oxidizes citric acid to acetone. Citric acid reduces ammoniacal silver nitrate only on strong heating. Citric acid is used for making beverages like lemonades, and Sharbats Some citrates like sodium, and potassium citrate are used in medicine as antacids, and as anticoagulants in blood transfusion. Ferric ammonium citrate is used for iron deficiency. Citric acid is also used as a mordant in dyeing and calico printing.

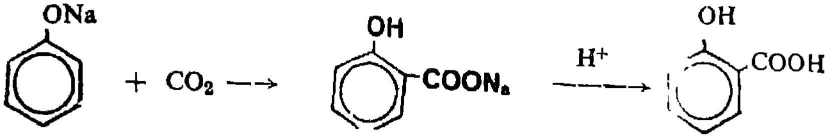
19.5-4 SALICYLIC ACID :



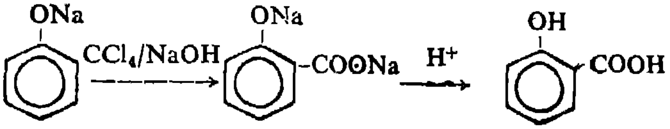
Salicylic acid is *ortho*-hydroxybenzoic acid. It occurs in many essential oils, e g. salicin, Its methyl ester is the main constituent of the oil of wintergreen.

Salicylic acid is commercially prepared from phenol by either of the followin two methods :

(i) *Kolbe's method :* Treatment of the salt of a phenol with carbon dioxide brings about substitution of the corboxyl group, $-COOH$ for hydrogen of the ring. This reaction is known as the Kolbe reaction In practice, dry powdered sodium phenate is heated at 400-415K with carbon dioxide under a pressure of six to seven atmospheres.



(ii) *Reimer-Tiemann reaction*. Sodium phenate heated with carbon tetrachloride in the presence of alkali also gives salicylic acid.



Properties :

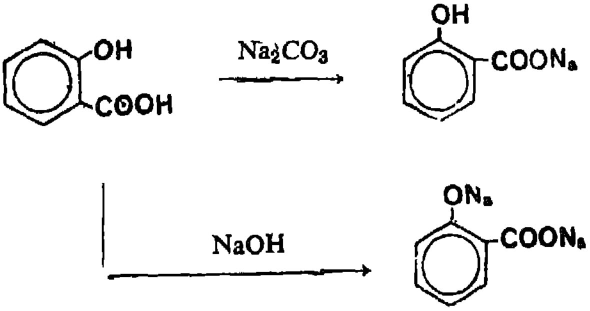
Salicylic acid is a colourless crystalline solid, m p 432K. It dissolves readily in hot water, alcohol and ether. Like the phenols, salicylic acid gives an intense violet colour with $FeCl_3$

Reactions :

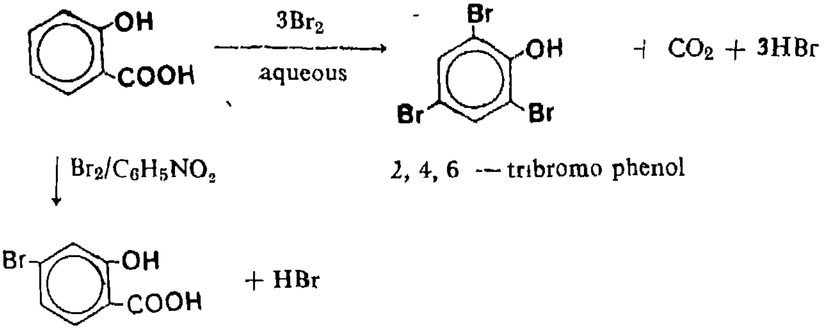
On heating at 485-495K, salicylic acid decomposes into phenol, and CO_2 In fact, all aromatic carboxylic acids which have electron donor groups like $-OH$ and $-NH_2$ undergo decarboxylation very easily.

Aromatic, carboxylic acids with electron withdrawing substituents like $-NO_2$ are more stable and undergo decarboxylation only when heated with a base.

Salicylic acid behaves both as a phenol and as a carboxylic acid. With Na_2CO_3 it forms a monosodium salt, and with NaOH, a disodium salt.

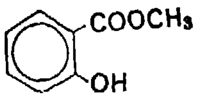


It gives acyl derivatives and esters It couples with diazonium compounds The action of bromine water on salicylic acid results in loss of CO_2 and formation of 2, 4, 6-tribromophenol Bromine in nitrobenzene solution however gives *o*-hydroxy-*p*-bromo-benzoic acid

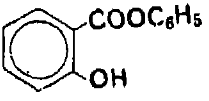


2, 4, 6 —tribromo phenol

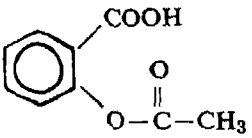
Salicylic acid and some of its derivatives are medicinally important Salicylic acid is used as an antiseptic and preservative Methyl salicylate is used in making perfumes and also in treatment of rheumatism Phenyl salicylate (salol) is used as an intestinal antiseptic, it passes through the stomach unchanged and is slowly hydrolyzed in the intestines. It is also used to coat the pills which are intended to pass through the stomach without dissolving. Acetyl salicylic acid, commonly called *aspirin*, is one of the earliest known analgesics (pain reliever) and antipyretic (fever reliever). It is prepared by acetylation of salicylic acid with acetic anhydride in the presence of a few drops of sulphuric acid



methyl salicylate



phenyl salicylate (salol)



acetyl salicylic acid (aspirin)

EXERCISES

19 1 Define and describe following terms :

(a) polypeptide
(b) protein

(c) zwitter ion
(d) antifreeze
(e) fats and oils
(f) soap
(g) rearrangement reaction
(h) isoelectric point
(i) benzoylation
(j) Fenton's reagent
(k) decarboxylation

19.2 In a solution of pH-11, will glycine exist as an anion or as a cation ?

19.3 Draw the structures of six isomeric glycols of formula $C_4H_{10}O_2$ and name each by the IUPAC system. What is tetramethylene glycol. Which one of these glycols will react with periodic acid.

19.4 Describe simple tests (chemical) that can be used to distinguish between :

(a) ethylene glycol and glycerol
(b) 1, 2-propanediol and 1, 3-propanediol
(c) 1, 3-propanediol and glycerol
(d) maleic acid and fumaric acid
(e) a mineral oil and a vegetable oil
(f) citric acid and tartaric acid
(g) acetic acid and chloroacetic acid
(h) glycine and lactic acid.

19.5 Write equations to show how lactic acid can be prepared from each of the following :

(a) acetaldehyde
(b) propionic acid
(c) propylene glycol

19.6 How are glycol and glycerol prepared (i) in the laboratory, (ii) industrially ?

19.7 Name the compounds and state the conditions under which they are formed when glycol is treated with

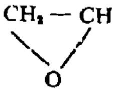
(a) Na (b) HBr (c) $KMnO_4$ (d) HNO_3 (e) $ZnCl_2$ (f) HIO_4

19.8 Point out the various uses of (a) glycol, (b) glycerol, (c) salicylic acid, and (d) citric acid.

19.9 Write down the products of following reactions :

$$\text{glycine} \xrightarrow{NaNO_2+H_2SO_4}$$

glycine + formaldehyde ⟶ ?



$+ CH_3CH_2OH \xrightarrow{H^+}$?

glycerol + Fenton's reagent ⟶ ?

glycerol + HI ⟶ ?

NaOH + CO ⟶ ?

19.10 Explain why:

(a) first dissociation constant of oxalic acid is much greater than second dissociation constant

(b) lactic acid and chloroacetic acid are stronger acids than acetic acid

19.11 Discuss the methods of preparation of glycine and tartaric acid.

19.12 How will you prepare

(a) aspirin from salicylic acid

(b) salicylic acid from phenol

(c) acetone dicarboxylic acid from citric acid

(d) oxalic acid from tartaric acid

(e) tartaric acid from succinic acid

(f) lactide from lactic acid.

UNIT 20

Biochemistry

We have studied simple organic molecules in the previous Units In the present Unit we shall study the molecules which form basis of our life and are complex in nature

20.1 LIVING SYSTEMS

Living creatures or organisms perform certain functions of life and have highly complex structures. For keeping themselves fit and functioning living organisms need energy and matter in various forms There are two main reasons why organisms need energy. Firstly most of the constituent compounds are made from environmental substances by free energy requiring reactions. Secondly, the body materials of animals and plants are all highly organised and are formed from raw materials by a decrease in entropy According to the general equation for free energy change, $\Delta G = \Delta H - T\Delta S$, every change involving decrease in entropy is accompanied by absorption of energy. Organisms have the capacity to extract and transform energy from their environment. They use simple raw materials to build and maintain their complex structures. The raw materials used by living organisms are called *nutrients* These are water, carbon dioxide, inorganic mineral salts and *foods* like starch, fats and some other organic matters. The energy needs may be met by either direct sunlight (as in green plants) or by the energy released by the assimilation of foods as in animals. Living organisms usually carry on their activities at or near body temperatures and at atmospheric pressures The medium for biochemical reactions is mainly water and has usually a pH of about 7. A living system is always at a steady state (not at thermodynamic equilibrium). Raw materials are taken in from the environment, some desired substances are made from these and waste substances are excreted in more or less a steady continuous manner. Finally, living systems have the capacity to *adapt* themselves to the natural environment.

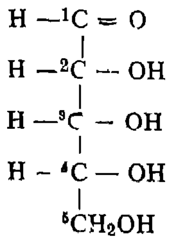
20.2 BIOMOLECULES

Living systems are composed of several complex life-less substances like carbohydrates, proteins, nucleic acids, lipids, etc., these compounds play specific functions In addition, some simple small molecules like vitamins and mineral salts also play an important role in the functions of organisms. These biomolecules interact with each other in very specific relationships These interactions constitute molecular logic of life processes. Apart from the biosubstances mentioned above, all living systems contain 70 to 90% water by weight. Some of the biomaterials involved in life processes are described in the sections to follow.

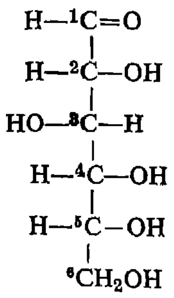
20.3 CARBOHYDRATES

Carbohydrates are so named since besides carbon they consist of hydrogen and oxygen in a ratio of 2 : 1 as in water itself They seem to be hydrates of carbon and can be represented by the general formula $C_x(H_2O)_y$ where x and y are whole numbers. If x is between 3 and 7, such carbohydrates are called simple sugars or *monosaccharides* The monosaccharides are further classified on the basis of number of carbon atoms in their molecules : C_3 sugars are called trioses, C_4 sugars tetroses, C_5 sugars pentoses, C_6 sugars hexoses and C_7 sugars heptoses The suffix *-ose* is used to denote sugars

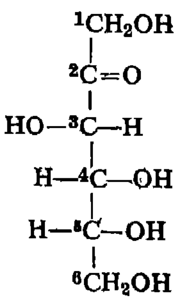
The monosaccharides are polyhydroxy compounds and are either aldehydes or ketones In aldehydic sugar the $>C{=}O$ group is the terminal group and in keto sugars it takes a position next to the terminal carbon. The aldehydic sugars are collectively called *aldoses* and the ketonic sugars, *ketoses*. The common aldoses are ribose (C_5 sugar) and glucose (C_6 sugar) and the most common ketose is fructose (C_6 sugar).



ribose

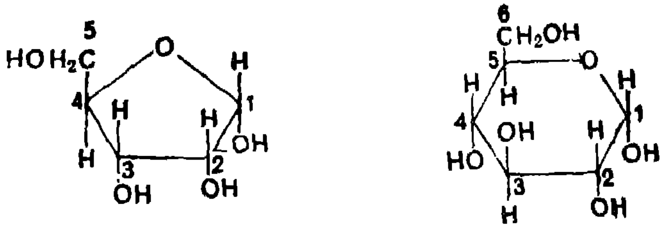


glucose



fructose

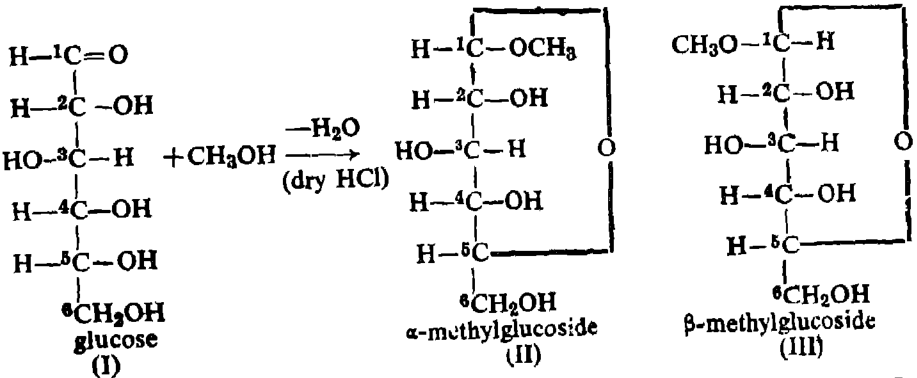
All monosaccharides have asymmetric carbon atoms and therefore exhibit optical activity Also, most of the naturally occuring sugars belong to the D-series and exhibit a property called mutarotation.* Mutarotation is the property of a sugar showing different optical rotation under different conditions This has been attributed to existence of sugar molecules in ring forms like furan (5 membered) and pyran (6 membered). In these structures the aldehydic group in aldoses and the ketonic group in ketose change to alcoholic groups and acquire asymmetric characters.



ribofuranose glucopyranose

(In these formulae there is a carbon atom at each numbered corner position.)

All the monosaccharides are soluble in water, have a sweet taste and char on heating. They give the usual chemical reactions characteristic of alcohols and of aldehydes or ketones. However, in presence of dry hydrogen chloride they exhibit an unusual reaction with other hydroxy compounds such as alcohols or phenols The products of these reactions are collectively called *glycosides*. Glucose gives rise to two glycosides with methyl alcohol which are called α-methylglucoside and β-methylglucoside** respectively.



glucose
(I)

α-methylglucoside
(II)

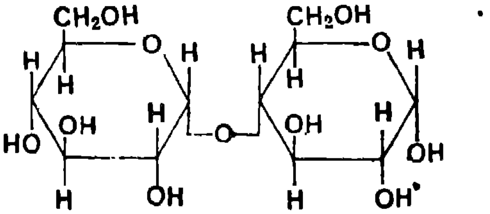
β-methylglucoside
(III)

---

* The specific rotation of sugar solutions changes with time till it acquires a constant value For example, the specific rotation of either α-glucose (+112°) or β-glucose (+19°) changes with time and acquires a constant value of +52.5°. This change in specific rotation of a sugar with time is known as mutarotation and is due to the formation of an equilibrium mixture of the two forms, α and β as a result of their interconversion through their open chain form.

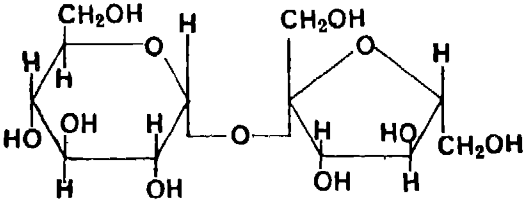
** *(See footnote on next page)*

By elimination of water molecules two or more identical or different monosaccharides may join together end to end to form chain-like larger molecular structures. If only two monosaccharide molecules are joined together, the new molecule belongs to a *disaccharide*. For example, if two glucose molecules are joined together the disaccharide, maltose or malt sugar, is formed; a combination of a glucose and a fructose molecule yields the disaccharide, sucrose; a combination of glucose and another hexose sugar, galactose, yields the disaccharide, lactose or milk sugar.



glucose unit glucose unit

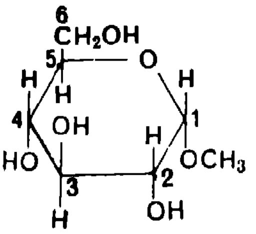
maltose



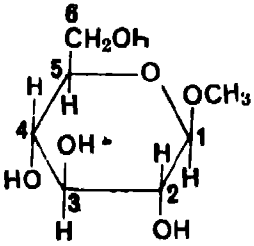
glucose unit fructose unit

sucrose

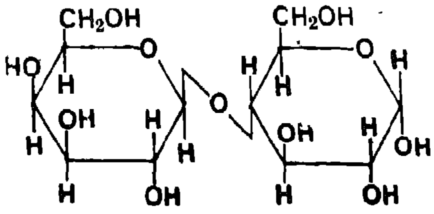
** The terms α-and β – refer to the position of the hydroxyl group on carbon – 1 in the molecule of sugar. In the case of methylglucoside, when the—CH_3 group is written to the right in the closed chain structure (II) or in down position in the hexagonal ring structure (IV), the molecule is assigned the α–configuration. Similarly when the—CH_3 group is written on the left in the closed chain structure (III) or in up position in the hexagonal ring structure (V), the molecule is assigned the β – configuration. Ordinary glucose is an equilibrium mixture of α-and β-forms.



α-methyl glucoside
(—OCH_3 group on C-1 is down)
(IV)



β-methyl glucoside
(—OCH_3 group on C-1 is up)
(V)



galactose unit glucose unit

lactose

The common disacccharides have the molecular formula $C_{12}H_{22}O_{11}$.

Formation of disaccharides from monosaccharides can be represented as

$$2\,C_6H_{12}O_6 \xrightarrow{-H_2O} C_{12}H_{22}O_{11}$$

Disaccharides can be easily hydrolyzed to give back the component monosaccharides. Thus cane sugar, sucrose, on being boiled under mild acidic conditions yields a mixture of glucose and fructose. Due to a strong laevorotatory character of fructose, the resulting mixture of glucose and fructose becomes laevorotatory. Cane sugar itself is dextro-rotatory in nature As the resulting mixture of sugars shows an inversion of optical rotation, this mixture is called *invert sugar*. Further, since fructose is about twice as sweet as cane sugar, the resulting invert-sugar gives extra sweetness to canned fruits and jams. (Relative sweetness of some of the common sugars is shown in Table 20.1).

TABLE 20.1

The Relative Sweetness of Some of the Common Sugars

Sucrose	100
Lactose	16
Maltose	33
Glucose	74
Fructose	173
Invert sugar	130

If more than two monosaccharide units are joined together, we get *polysaccharides* In fact, polysaccharides are said to be polymers of simple sugars. Polypentoses

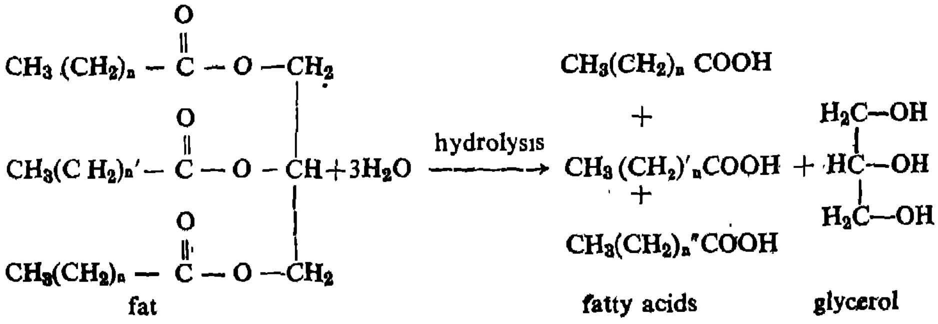
$(C_5H_8O_4)_x$ are called pentosans and polyhexoses are called hexosans $(C_6H_{10}O_5)_x$. The animal polysaccharide, glycogen, which occurs in muscles and in liver, is a polymer consisting of hundreds to thousands of glucose units. The plant polysaccharide, cellulose, which is present in the cell walls of the plant cells, consists of upto 2,000 glucose units. Another plant polysaccharide, starch, which occurs in the cereal grains wheat, rice, etc., consists of two polymers amylose and amylopectin ; each has about 500 to 1000 glucose units.

Carbohydrates function in two ways They are either *structural* components of cells or function as chief *bio-fuels* to provide energy for the functioning of living systems. The monosaccharide, glucose, obtained by the hydrolysis of starch or glycogen, is the chief form in which carbohydrates are transported from cell to cell in all organisms and over longer distances by sap in plants and by blood in animals.

Starch is easily hydrolyzed in presence of enzymes of human and animal digestive systems Hydrolysis of cellulose needs enzymes of a different kind These are present in the digestive systems of grazing animals and hence they can use cellulose of grass and plants as food by converting it to glucose.

20.4 LIPIDS

Fats and their derivatives occuring in living systems are collectively known as *lipids*. These lipids are insoluble in water but soluble in organic solvents like chloroform and carbon tetrachloride. Most of the fats are glycerol esters of unbranched long chain carboxylic acids having an even number of carbon atoms. They can be hydrolyzed to yield glycerol and the acids. These straight chain acids because of their occurence in fats, have been called *fatty acids*.

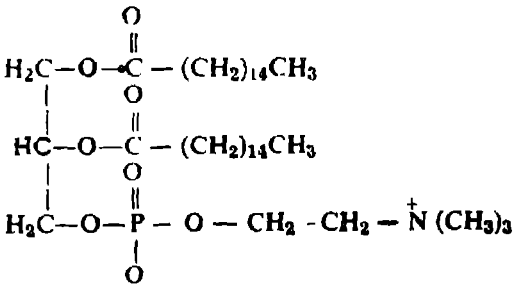


$$\begin{array}{l} CH_3(CH_2)_n-\overset{\overset{\large O}{\|}}{C}-O-CH_2 \\ \qquad\qquad\qquad\qquad\quad | \\ CH_3(CH_2)_n'-\overset{\overset{\large O}{\|}}{C}-O-CH+3H_2O \\ \qquad\qquad\qquad\qquad\quad | \\ CH_3(CH_2)_n''-\overset{\overset{\large O}{\|}}{C}-O-CH_2 \\ \qquad\qquad \text{fat} \end{array} \xrightarrow{\text{hydrolysis}} \begin{array}{c} CH_3(CH_2)_n\,COOH \\ + \\ CH_3(CH_2)'_nCOOH \\ + \\ CH_3(CH_2)_n''COOH \\ \text{fatty acids} \end{array} + \begin{array}{c} H_2C-OH \\ | \\ HC-OH \\ | \\ H_2C-OH \\ \text{glycerol} \end{array}$$

Palmitic acid, $CH_3(CH_2)_{14}COOH$ and stearic acid, $CH_3(CH_2)_{16}COOH$ are the most common saturated fatty acids occuring in plants and animals. Unsaturated fatty acids, having one or more double bonds, also occur in natural fats. The most widely distributed unsaturated fatty acid is oleic acid, $CH_3(CH_2)_7-CH=CH-(CH_2)_7COOH$ Other unsaturated acids occurring in vegetable oils are linoleic acid $CH_3(CH_2)_4-CH=CH-CH_2-CH=CH-(CH_2)_7COOH$ and linolenic acid $CH_3CH_2-CH=CH-CH_2-CH=CH-CH_2CH=CH(CH_2)_7COOH$

Fats and fatty acids are important modes of *food storage* in living organisms. They are even richer sources of energy than carbohydrates. Fats present in the subcutaneous tissue of animals also act as good heat insulators and as shock absorbing-pads They may also play the role of *structural* components of cell membranes

Phospholipids are derivatives of fats in which only two of the glycerol —OH groups are esterified by fatty acids and the third one is estrified by some derivative of phosphoric acid An example is *lecithin*



lecithin

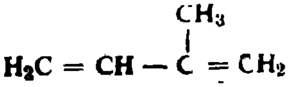
Phospholipids are usually present in the cell membranes

Waxes are a group of substances related to fats. They are fatty acid esters of long chain monohydric alcohols,

20 5 VITAMINS

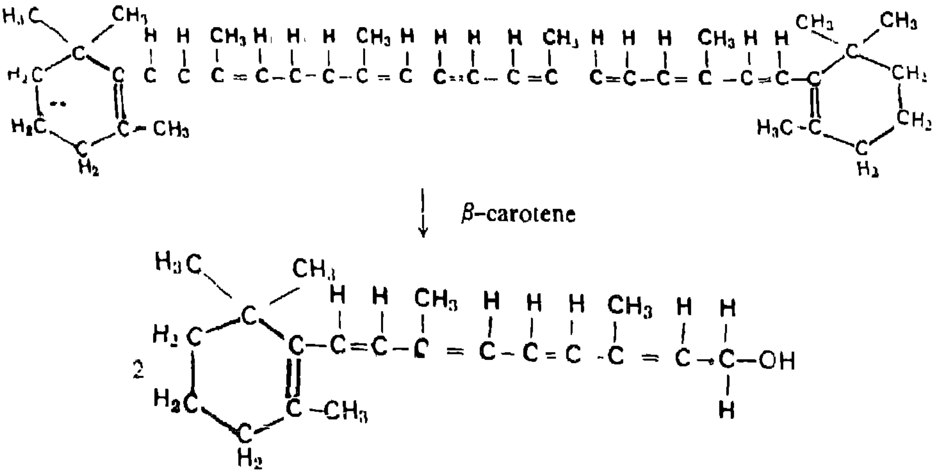
20 5-1 CAROTENOIDS—VITAMIN A

It is another group of related compounds which are polymers of the hydrocarbon, *isoprene*,



$$H_2C=CH-\overset{\displaystyle CH_3}{\overset{|}{C}}=CH_2$$

These compounds are oil-soluble pigments and they produce red, orange, yellow and brown colours in both animal and plant materials Carotenoids include carotenes and xanthophylls Carotenes occur in tomatoes, pumpkins, carrots, egg yolk, milk, butter and some other materials Vitamin A is a carotene derivative.

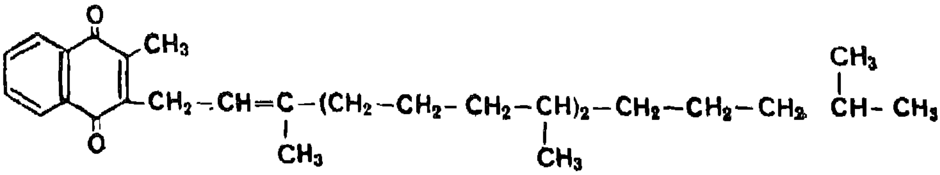


vitamin A

A deficiency of vitamin A in growing animals results in retarded growth and a change in epithelial cells. The corneas of eyes become opaque, leading to a condition called *xerophthalmia* Another observation is the drying up of skin. This condition is known as *xerosis* The deficiency of vitamin A also causes night blindness

20.5-2 OTHER VITAMINS

Vitamin K, which is present in leafy vegetables, plays a vital role in the coagulation properties of blood Vitamin E (α-tocopherol), often called the "antisterility" vitamin, is responsible for normal reproduction functions. Vitamin E is found in animal and vegetable oils, cottonseed oil, corn oil, peanut oil, etc Vitamin D plays an important role in the development of bones and teeth in growing children. Rickets is a disease caused by deficiency of vitamin D and leads to legs curved like bows and poor formation of teeth. This deficiency can be overcome by the supply of foods like milk, eggs and liver meat which are rich in vitamin D. Structures of these vitamins are given below



vitamin K*

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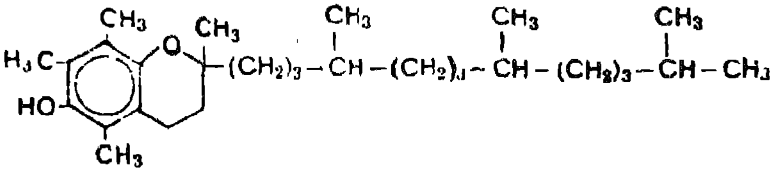
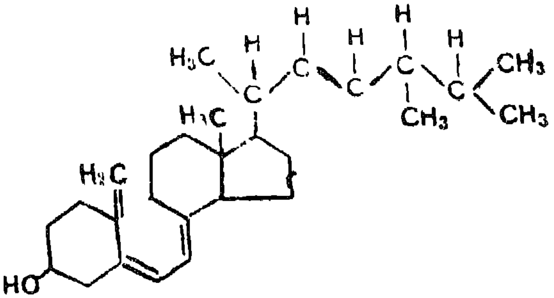
* Vitamin K is of two types, K_1 and K_2. The above given structural formula is of vitamin K_1.



Vitamin E

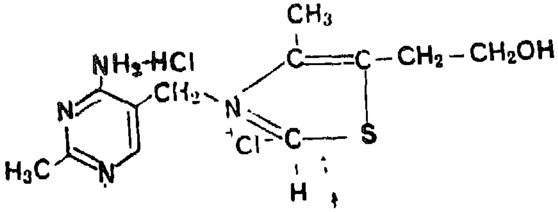


Vitamin D_2

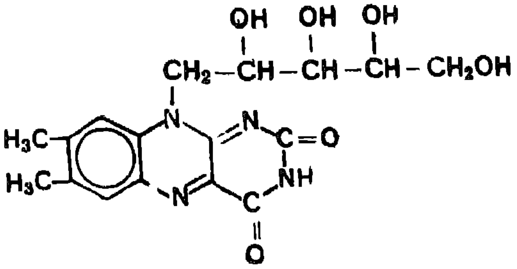
Vitamin B-complex consists of a number of substances of various complexities. The more important of these are described below

Thiamine or vitamin B_1 is available in milk, vegetables, yeast and rice polishings. Lack of this component in diet causes loss of appetite and the disease beriberi

Riboflavin or Vitamin B_2 is also available from milk, vegetables and rice polishings. Its absence from food leads to sore tongue and skin disorders.

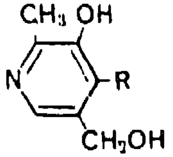


thiamine hydrochloride



riboflavin

Vitamin B_6 consists of three closely similar components one of which is called *pyridoxine* These components are available from cereal grains Prolonged deficiency of vitamin B_6 may cause nervous disturbances and convulsions.



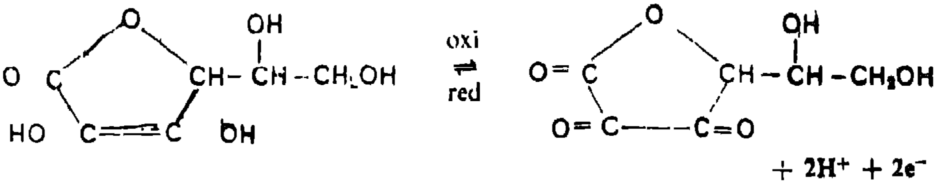
R = $-CHO$ pyridoxal

R = $-CH_2OH$ pyridoxine

R = $-CH_2NH_2$ pyridoxamine

Vitamin B_{12} is a *cyanocobalamin* with a large complex molecule It has a cobalt atom co-ordinated to four nitrogen atoms This vitamin occurs only in animals and micro-organisms but not in plants. Presence of vitamin B_{12} in rain water is attributed to micro-organisms sucked up by winds. Our daily need of this vitamin is very small (about 1.5 microgram). Lack of this vitamin causes a bad form of anaemia

Vitamin C or ascorbic acid occurs in fresh vegetables and fruits, particularly tomatoes, chillies, amla, citrus fruit (lemon, oranges), papita, etc. Absence of this vitamin causes the disease scurvy It undergoes reversible oxidation :

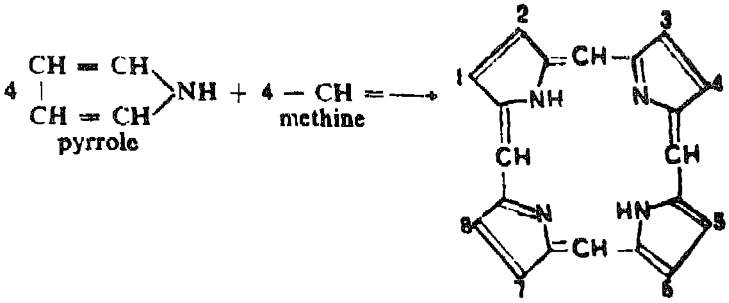


ascorbic acid dehydroascorbic acid

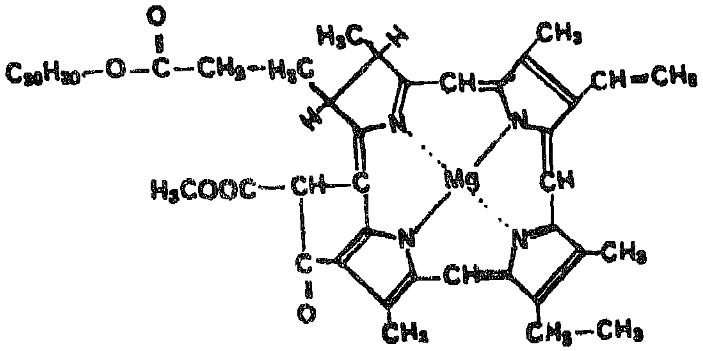
Vitamin C is destroyed on contact with oxygen of air even at room temperature. It loses effectiveness under open storing. Vegetables lose major part of their vitamin C content when cooked in contact with air in open pans for long periods of time. Cooking of vegetables in closed pans or pressure cookers and storing of vitamin C tablets in sealed strip foils is considered desirable Cooking in presence of sodium bicarbonate (baking soda) also causes a quicker loss of vitamin C as it is more easily oxidized in alkaline than in acidic media.

20.6 TETRAPYRROLES OR PORPHYRINS

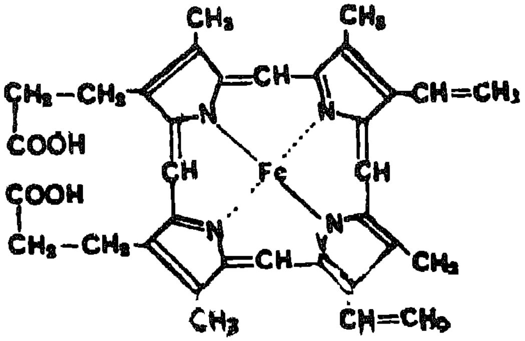
Biochemically important compounds, chlorophyll, haemoglobin and cytochromes have in common a cyclic structure in which four pyrrole units (C_4NH_5) are linked by four methine bridges (—CH =) as shown below



On this basic structure appropriate substituents can be introduced to get the different derivatives e g. chlorophyll and haeme



Chlorophyll (a green pigment of plants



Haeme (part of haemoglobin responsible for carrying oxygen in blood

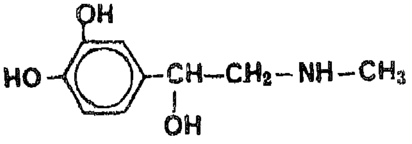
20.7 HORMONES

Hormones are chemical substances which are made in ductless (endocrine) glands. They move to different parts of the body through the blood stream and exert strong regulatory influence on the chemical processes taking place there. A disturbance of hormonal balance may lead to abnormal metabolic processes. Some of the hormones are shown in the following table.

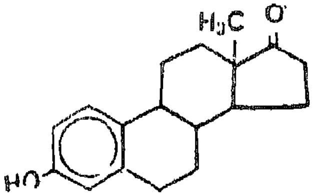
TABLE 20.2

Hormones in Man

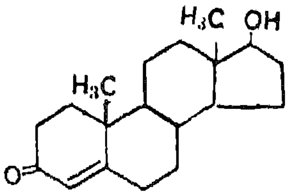
Name	*Organ of Secretion*	*Function*
Adrenaline (Epinephrine)	Adrenal medulla	Increases pulse rate and blood pressure ; releases glucose from glycogen and fatty acids from fats
Testosterone	Testis	Normal functioning of male sex organs
Estrone and Estradiol	Ovary	Normal functioning of female sex organs
Insulin	Pancreas	Metabolism of glucose
Cortisone	Adrenal cortex	Metabolism of water, mineral salts, fats, proteins and carbohydrates
Pituitary hormone	Pituitary gland	Stimulation of adrenal cortex thyroid gland, testis, ovaries and mammary glands



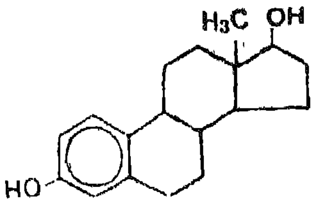
epinephrine



estrone



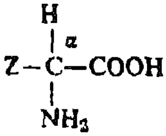
testosterone



estradiol

20 8 PROTEINS

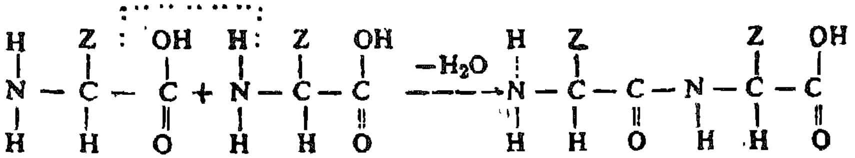
These compounds are polymerization products of amino-acids. The general formula of an amino acid is



$$\begin{array}{c}H\\ |\,\alpha\\ Z-C-COOH\\ |\\ NH_2\end{array}$$

where $-NH_2$ is an amino group, $-COOH$ a carboxyl group, and **Z**, a group which can considerably vary in composition in various amino acids There are about 20 naturally occuring amino acids All of them contain amino and carboxyl groups attached to the $\alpha-$carbon atom The simplest amino acid is glycine where $Z=H$; if $Z=CH_3$, the amino acid would be alanine. Since there is an asymmetric carbon atom present in all amino acids except glycine, amino acids show optical activity and most of them occurring in cells are of L-type. All the sugars occurring in nature are of D-type.

In proteins, the adjacent amino acids are joined in such a way that the amino group of one acid links with the carboxyl groups of its neighbour forming an imide bond The imide bonds in proteins are called *peptide bonds.*



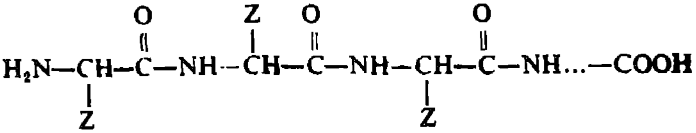
$$\begin{array}{ccccccccccccccccccccccc}H & & Z & & OH & & H & & Z & & OH & & & H & & Z & & & & & & Z & & OH\\ | & & | & & | & & | & & | & & | & & -H_2O & | & & | & & & & & & | & & |\\ N & - & C & - & C & + & N & - & C & - & C & & \longrightarrow & N & - & C & - & C & - & N & - & C & - & C\\ | & & | & & \| & & | & & | & & \| & & & | & & | & & \| & & | & & | & & \|\\ H & & H & & O & & H & & H & & O & & & H & & H & & O & & H & & H & & O\end{array}$$

The link between C and N in $-\underset{\underset{\displaystyle O}{\|}}{C}-\underset{\underset{\displaystyle H}{|}}{N}-$ bond is a peptide bond

If two amino acids are joined by a peptide bond the new unit is called a ***dipeptide.*** If many aminoacids are joined by means of peptide bonds, the whole chainlike complex is called a ***polypeptide.***

The polypeptides can vary in an unlimited fashion. Firstly, they can contain any one or all of the different naturally occurring amino acid. Secondly, they can contain almost any number of each of these amino acids; and thirdly, the specific sequence in which given numbers and types of amino acids are joined as a chain can vary almost without any restriction. When three types of amino acids are combined as in a tripeptide the number of possible permutations is $3!$ or $1 \times 2 \times 3 = 6$. For example, if A represents alanine, G, glycine and T, tryptophan, the six isomers may be indicated by AGT, ATG, GAT, GTA, TAG, and TGA. Likewise, a decapeptide in which all the amino acids are different can have 3,628,800 structural isomers. In other words, amino acid units can be envisaged to represent an "alphabet" of 20 letters and an astronomically large number of different polypeptide 'words' can be constructed from this alphabet.

The possible number of chemically different proteins is astronomical. Indeed, no two organisms have exactly the same type of proteins. Every polypeptide chain will have a free amino group and a free carboxyl group at the two ends. Thus a polypeptide may be represented as :



$$H_2N-\underset{\underset{Z}{|}}{CH}-\overset{\overset{O}{\parallel}}{C}-NH-\overset{\overset{Z}{|}}{CH}-\overset{\overset{O}{\parallel}}{C}-NH-\underset{\underset{Z}{|}}{CH}-\overset{\overset{O}{\parallel}}{C}-NH...-COOH$$

If a line is drawn through the Z-groups of the consecutive amino acids in the chain this line would resemble a helical or a spiral structure (Fig 20.1)

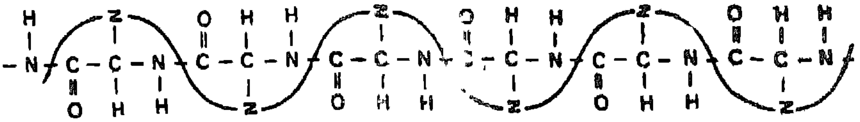


Fig. 20.1 Structure of a polypeptide. Formula emphasises a helical structure.

The spiral structure of a protein : A line connecting the Z-groups of consecutive L-amino acid units in the polypeptide chain forms a spiral called an α-helix. The α-helix is held together by hydrogen bonds between the H of-NH of one amino acid and O of C=O in another amino acid, three units distant. On an average there are 3.7 amino acid units per turn of the spiral.

If long coiled thread-like stucture of this sort remain extended as a strand the protein is known as fibrous. Hair, hoofs, skin, nails, silk, fibroin, muscle protein and wool are examples of fibrous proteins. However, there are many proteins in which the coils are looped, twisted and folded back on themselves forming ball like three-dimensional configurations. These proteins are said to be *globular*.

The globular proteins are very important for living systems since they act as catalysts for chemical reactions taking place in body cells. These catalysts are called *enzymes* and each enzyme often catalyzes only one particular reaction Whereas many organic chemical reactions conducted in the laboratory require organic solvents, high temperatures and pressures, the reactions in a living system are carried out in water medium, often at room temperature and atmospheric pressure and under neutral conditions. Thus the biosynthesis and the mechanism of action of enzymes is an *important* field of study in biochemistry. Proteins also represent vital *construction materials* out of which the *basic framework* of cells is build up.

Proteins are quite sensitive to actions of heat and chemicals. These may change the spatial arrangement of a protein molecule Often soluble forms of proteins such as globular protein, are converted to the fibrous or insoluble forms White of raw egg is a globular protein. When the egg is boiled hard, the protein takes the insoluble fibrous form and the protein is coagulated Such changes of spatial structure of proteins which are generally irreversible are known as *denaturation of protein* Addition of concentrated acids and bases and heavy metal ions (Hg, Ag ions) can also cause coagulation and denaturing of proteins Denatured proteins can no longer participate in biological activities This is also the reason for enzymes becoming ineffective when heated. Enzymes have complex protein structure.

20.9 DIGESTION OF FOOD

The digestion of food substances such as polysaecharides, proteins and fats takes place in different parts of the alimentary tract and is achieved by *mechanical* as well as *chemical means.* Mechanical actions of chewing and mixing occuring in the stomach lead to subdivision of food materials into smaller particles and their suspension in water Chemical actions then reduces these particles to small molecular dimensions which can be absorbed into the blood stream from the intestine. These are mainly assisted by the enzymes present in the different parts of the food track. The digestive reaction can be written as:

$$\text{Food} + \text{water} \xrightarrow{\text{enzyme}} \text{small molecules.}$$

In mammals the enzymatic digestion occurs mainly in mouth, stomach and small intestine. At each of these sites, specialized digestive glands secrete one or more digestive juices. First, as the food material enters the mouth, the salivary glands present produce *saliva* which contains the enzyme called amylase or ptyalin. This is responsible for the hydrolysis of polysaccharides such as starch to maltose.

From the mouth, food passes into the stomach, Here it mixes with *gastric juice* which contains strong hydrochloride acid (pH 2.0) and a proteolytic enzyme, pepsin.

This enzyme hydrolyzes proteins to amino acids and small peptides. The hydrochloric acid coagulates the proteins and also facilitates the action of pepsin.

In the small intestine, particularly in its section next to the stomach, digestion of all types of foods occurs. Here the food mixes with *intestinal juice* secreted by the gut wall, *pancreatic juice* from the pancreas and *bile* from the liver; and also reaction medium changes from acidic to alkaline (pH 7.5). The carbohydrates are acted upon by amylases and converted to simple monosaccharides. Lipids are emulsified by the bile and converted to fatty acids and glycerine by the lipases. Proteinases like pepsin, trypsin and chymotrypsin, convert proteins to simple amino-acids.

When the digestion is completed, the intestine contains water, dissolved mineral ions, monosaccharides, amino acids, fatty acids, glycerin, vitamins, etc These are absorbed into the blood stream through the intestinal wall. The undigested or un-digestable components of food are propelled further into the large intestine and excreted.

$$\text{Proteins} \xrightarrow[\text{chymotrypsin}]{\substack{\textit{proteinases}\\ \text{pepsin, trypsin}}} \text{polypeptides} \xrightarrow{\substack{\textit{peptidases}\\ \text{(intestinal)}}} \text{amino acids}$$

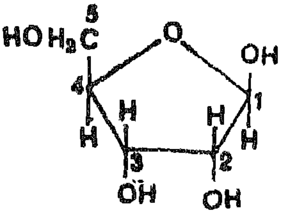
$$\text{Polysaccharides} \xrightarrow[\text{intestinal)}]{\substack{\textit{amylases}\\ \text{(salivary, pancreatic,}}} \text{disaccharides} \xrightarrow[\text{intestinal)}]{\substack{\textit{disaccharases}\\ \text{(salivary, pancreatic}}} \text{monosaccharides}$$

$$\text{Fats} \xrightarrow{\text{bile salts}} \text{emulsified fat} \xrightarrow[\text{intestinal)}]{\substack{\textit{lipases}\\ \text{(gastric, pancreatic,}}} \text{fatty acids, glycerin.}$$

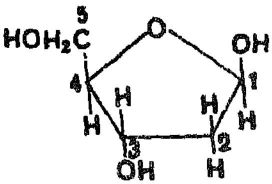
20.10 NUCLEOTIDES

A *nucleotide* consists of three parts: a phosphate group, a pentose sugar and a nitrogenous base. The pentose sugar may be either ribose or deoxyribose and the nitrogenous base may be any one of the two purines (adenine and guanine), or the three pyrimidines (thymine, cytosine and uracil). According to the type of pentose present, the nucleotides can be of two types, *ribonucleotides* and *deoxyribonucleotides*.

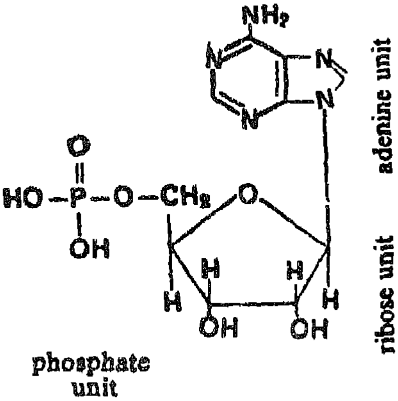
The carbohydrate derivatives of purines or pyrimidines are called *nucleosides*. The nucleosides are named after the bases. Thus riboside of adenine is called adenosine and the deoxyriboside is called deoxyadenosine.



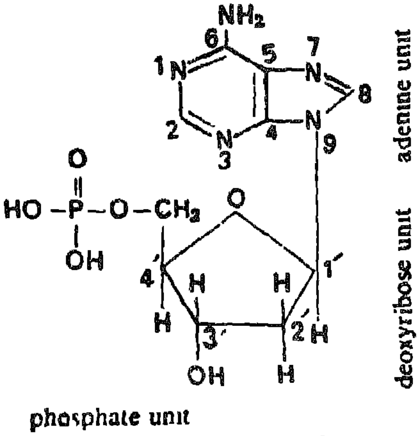
β-D-ribose



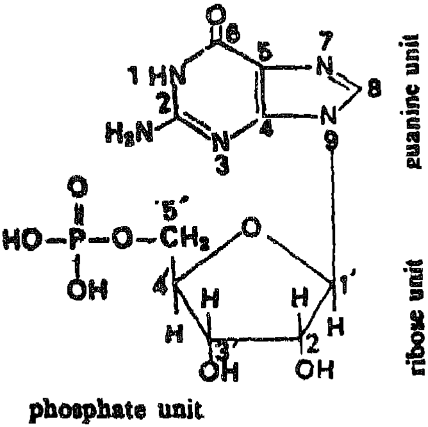
β-D-2-deoxyribose



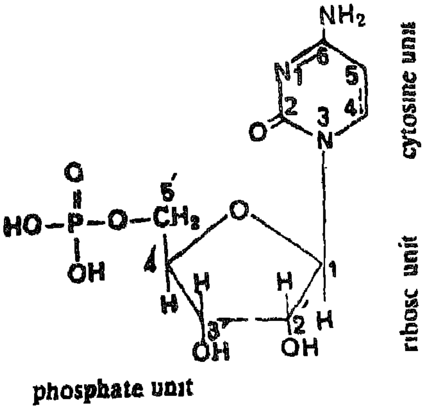
Adenine ribonucleotide, adenylic acid or adenosine 5′-monophosphate (AMP)



Adenine deoxyribonucleotide,* deoxyadenylic acid or deoxyadenosine 5′-monophosphate (d-AMP)



Guanine ribonucleotide, guanylic acid or guanosine monophosphate (GMP)



Cytosine ribonucleotide, cytidylic acid or cytidine monophosphate (CMP)

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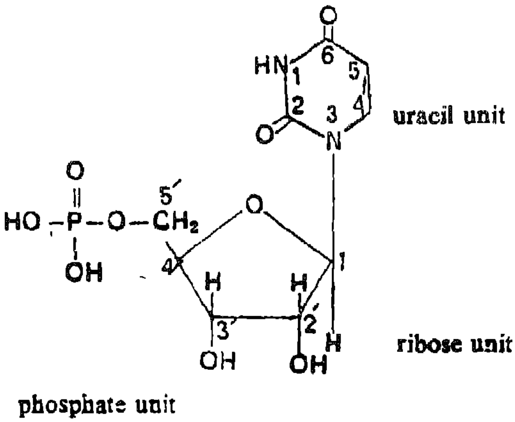
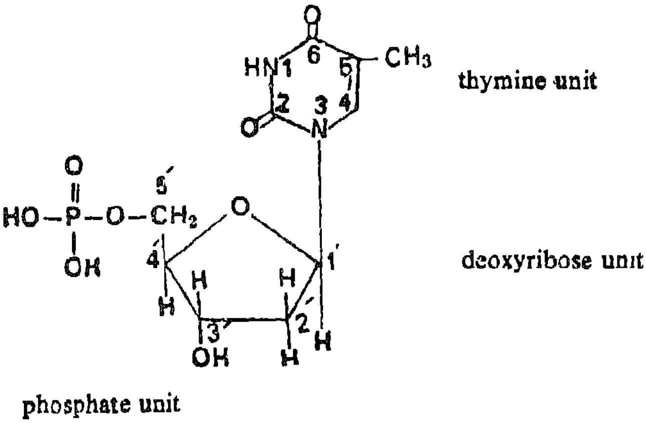
*In adenine deoxyribonucleotide, the pentose is 2-deoxyribose in which two H atoms are present on the second carbon atom.



Uracil ribonucleotide, uridylic acid
or uradine monophosphate (UMP)

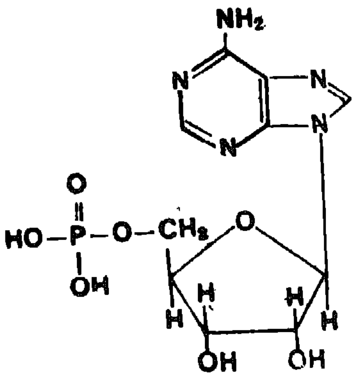


Thymine deoxyribonucleotide,
thymidylic acid or thymidine
monophosphate (TMP)

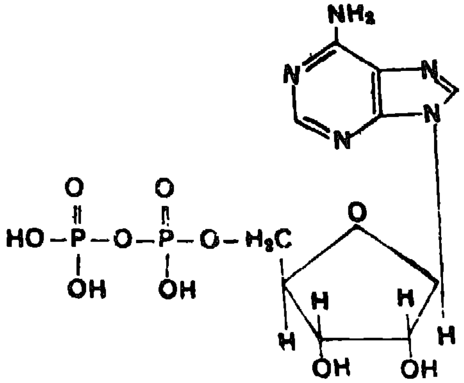
Nucleotides are building blocks of large molecules. They serve three crucial functions in cells. Some are *energy carriers*, others are *co-enzymes* and still others are carriers of hereditary information (*genetic code*).

Energy Carriers

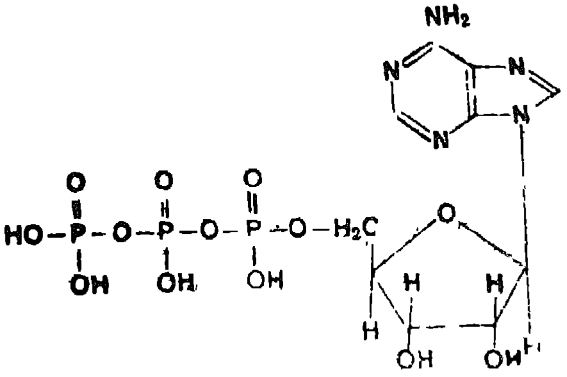
A nucleotide can link up in a serial fashion with one or two additional phosphate groups. For example, if to adenosine-monophosphate (AMP) one more phosphate group is added, then adenosine diphosphate (ADP) is formed. If two phosphate groups are added to AMP, adenosine triphosphate (ATP) will be formed.



AMP
(A-R-P)



ADP
(A-R-P-P)



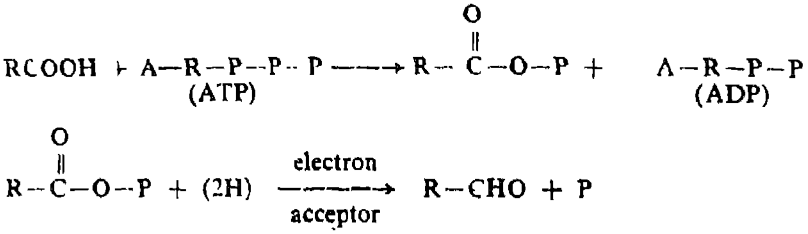
ATP
(A-R-P-P-P)

(The symbols A, R and P represent adenine, ribose and phosphate respectively)

$$\underset{\text{(ATP)}}{A-R-P-P-P} + H_2O \longrightarrow \underset{\text{(ADP)}}{A-R-P-P} + P; \quad \Delta G_{25}(\text{pH } 7.0) = -31.8 \text{ kJ}$$

$$A-R-P-P + H_2O \longrightarrow A-R-P + P, \quad \Delta G_{25}(\text{pH } 7.0) = -31.8 \text{ kJ}$$

The energy carriers, ATP and ADP are actually phosphate anhydrides and when they are hydrolyzed release free energy and for their synthesis from AMP and ADP respectively require not only phosphate but also additional amount of energy This energy for their synthesis is derived in cells from oxidation of fuels such as carbohydrates and fats and the primary function of respiration actually is to produce ATP from ADP. *ATP is the most important energy carriers in all living cells.* Derivatives of other nucleotides (UTP CTP, GTP, TTP) play only a limited energy carrying role An example of how ATP participates in a set of reactions can be given. It is almost thermodynamically impossible to reduce a carboxylic acid to the corresponding aldehyde under biological conditions (i e. at room temp . pH = 7.0). Nevertheless living systems can accomplish this reaction in water medium by first increasing the energy content of the acid with the help of ATP and then reducing it to aldehyde



$$\underset{}{RCOOH} + \underset{(ATP)}{A{-}R{-}P{-}P{-}P} \longrightarrow R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}P + \underset{(ADP)}{A{-}R{-}P{-}P}$$

$$R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}P + (2H) \xrightarrow[\text{acceptor}]{\text{electron}} R{-}CHO + P$$

20.11 COENZYMES

Some enzymes are conjugated proteins; a non-protein group is attached to the protein moiety The non-protein portion, often called *prosthetic group* may be a metal or an organic group (usually a B-vitamin) or an organic group which includes a metal also. The complete conjugated protein is called *holoenzyme*, the proteinaceous part *apoenzyme* and the non-protein group is called *coenzyme* when it is a B-vitamin or *cofactor* (when it is a metal).

Holoenzyme $\rightleftharpoons$ Apoenzyme + Coenzyme

or Conjugate protein enzyme $\rightleftharpoons$ Protein + Prosthetic group

The proteinaceous part, apoenzyme, is characterized by its being heat labile and the coenzyme (prosthetic group) by its heat stability. For the active functioning of an enzyme both the proteinaceous part and the prosthetic group are essential.

In most coenzymes, the nitrogen base of nucleotide is replaced by another chemical unit usually a derivative of a particular B-vitamin. Some coenzymes do not have any nucleotide attached to them.

All the water-soluble B-vitamins are to be supplied in the diet. For example, a deficiency of nicotinamide in the diet results in a disease known as *pellegra* in humans and *black tongue* in dogs.

20.12 NUCLEIC ACIDS

Nucleic acids are *polynucleotides* having, upto thousands of linked nucleotide units. There are two types of nucleic acids depending upon whether they belong to ribose series or deoxyribose series. A system consisting of ribotides is *ribose nucleic acid* (RNA) and a system consisting of *deoxyribotides* is *deoxyribose nucleic acid* (DNA). DNA is the "master molecule" contained in the chromosomes of the cell nucleus. It is responsible for the inheritance of genetic characteristics of a particular species of a living organism. RNA and DNA are identical in structure except in two respects: whereas RNA has ribose as sugar and uracil as base (no thymine), DNA has 2-deoxyribose as sugar and thymine as base (no uracil) in their structures.

20.12-1 STRUCTURE OF DNA

In the DNA molecule, the phosphodiester bridges link successive nucleotides between the 5′-carbon atom of the deoxyribose of one nucleotide with the 3′-carbon atom of the next as shown in Fig. 20.2.

Thus the covalent backbone of DNA consists of alternate phosphate and deoxyribose units from which extend side chains consisting of the four different nitrogenous bases in a characteristic sequence. Since the difference is only in respect of the four nitrogenous bases (adenine, guanine, cytosine and thymine) and

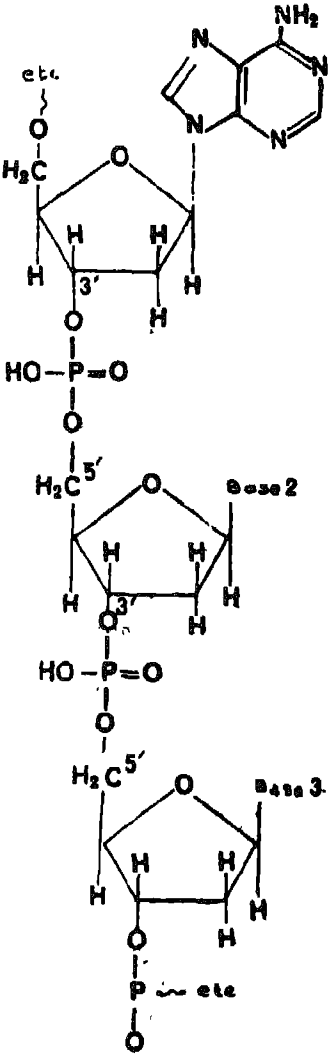
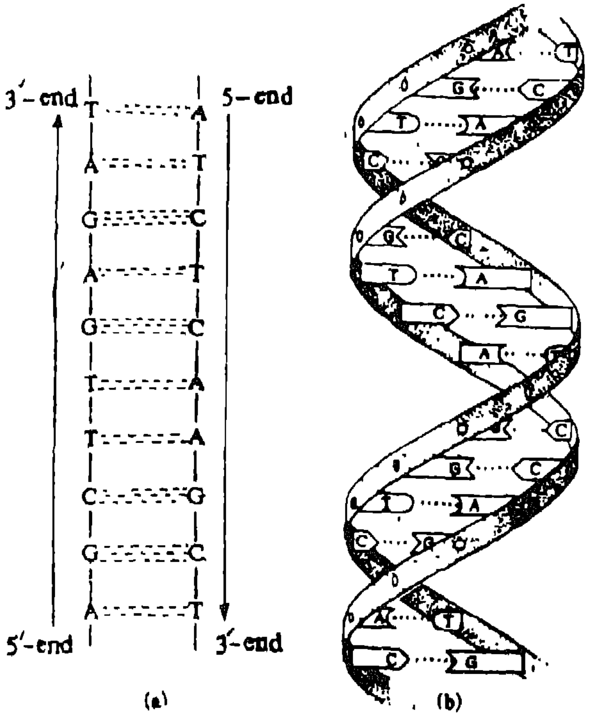


Fig. 20.2 Covalent backbone structure of DNA

the remaining parts (phosphate and deoxyribose) are common in the DNA polynucleotide. the genetic message that is imparted by DNA lies in the *specific sequence of the bases arranged* along the chain. A sample sequence would be A — T — C — G — A — G — C — T — C It is obvious that a very large number of different sequences is possible since most DNA molecules are very long with millions of nucleotide units For example, the chromosomes of bacterium, *E. Coli*, contains about 4,200,000 units of base pair and is only 1 2 mm long.

From X-ray data Watson and Crick found in 1953 that the native DNA as it exists in living systems has a right handed double helical structure called α—helix In this the two strands of DNA are intertwined helically around each other in such a way that the two molecules run in opposite directions and the bases of two strands fit each other in a *complementary* manner (Fig 20.3). For a close fit of the



(a) (b)

Fig 20 3 (a) Base pairing by optimum hydrogen bonding and complementary chain in DNA molecule.

(b) Representation of a double helix DNA molecule. (The vertical dotted lines between two bases represent hydrogen bonds The two strands in DNA molecule are shown in opposite direction i.e antiparallel).

two chains, it is found that adenine of one chain always pairs with thymine of the other chain and guanine of one chain pairs with cytosine of the second chain The pairing involves hydrogen bonds. When such pairing of the bases between the two strands of DNA occurs, both the strands of DNA are said to be *complementary* to each other. A simple diagram of the double helical DNA is illustrated in Fig 20.3. The designations "5′—end" and "3′—end" indicate the ends of the chain bearing a free hydroxyl group on the terminal deoxyribose unit at 5′ and 3′ positions respectively. (The letters A, G, C, T stands for adenine guanine, cytosine and thymine respectively) The macromolecule, DNA performs three functions which make it the universal key to life. First, the DNA provides the cell with information and instructions on how to *manufacture specific proteins* and through this control of protein manufacture, DNA controls the entire structcral and functional make up of the cell Second, cellular DNA has the unique properry *of precise self-replication.* DNA is a reproducing molecule. Self-replication property of DNA is at the root of all reproduction processes and in a basic sense even the reproduction of a whole plant or animal. Third, under certain conditions (for example, by the action of γ-rays, X-rays, ultraviolet light and some chemicals), DNA can undergo *mutations*, or become slightly or permanently altered in its nitrogenous base sequence As a consequence, the structural and functional traits can become different and these changes will be reflected in all the cells of the organism and its progency An example of mutation is *albinism* in which the pigmentation of skin, hair, etc. is affected. Finally, although the content of a cell in respect of other molecules may change according to environmental conditions, the DNA content of a cell is always constant

The structure of RNA is very similar, to that of DNA except in two respects, first, the sugar in RNA is ribose and not deoxyribose, and second, RNA is a single stranded molecule The structure of RNA is shown in Fig. 20.4. There are three different kinds of RNA molecules in a cell which are involved in specific protein biosynthesis, namely messenger RNA (m-RNA), ribosomal RNA (r-RNA) and transfer or soluble RNA (t-RNA). The messenger RNA (as its name implies) is a complementary copy of a segment of one strand of DNA and has a very short life. [For example, if the segment of the strand of DNA has the base sequence, A — T — C — G — A — A — T — T — , the m-RNA base sequence would be — U — A — G — C — U — U — A — A —. In other words, m-RNA carries the message of DNA for the specific protein synthesis as and when required. The ribosomal RNA is the site of protein synthesis in the cytoplasm and carries no message of DNA. The transfer RNA is a small molecule and as its name implies, it transfers amino acid to the site of protein synthesis. There are at least twenty different t-RNA molecules each specific for one amino acid

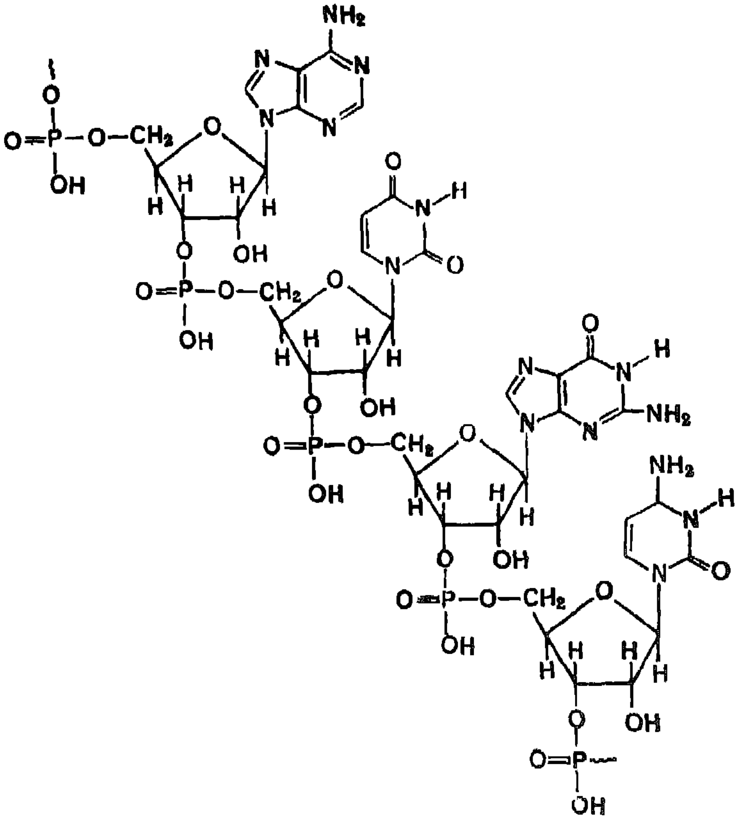


Fig. 20.4 Structure of RNA (only a part of RNA molecule is show here)

20.12-2 VIRUSES

Diseases like the common cold, measles, small pox, influenza, poliomyelitis and several others are attributed to specific substances called viruses. Each virus consists of two major parts : a core of a nucleic acid which may either be DNA or RNA and a protein covering which protects the core and helps the virus to penetrate a cell wall. Once the virus DNA or RNA penetrates a cell wall, it compels the cell organization to reproduce the virus particles like itself. When their number increases sufficiently, the original cell bursts. The new virus particles now start the destruction of new host cells.

20.13 BIOSYNTHESIS OF PROTEINS

In a cell, the molecular elements, DNA, RNA and proteins interact in such a way that the flow of genetic information under usual circumstances proceeds from

DNA of the parent cell to DNA of the daughter cells, and, within any given cell, from DNA to RNA to protein, according to the overall scheme.

$$\begin{tikzcd}
\text{Parent Cell} & DNA \arrow[r, "A"] \arrow[d, "R"] & RNA \arrow[r, "B"] & \text{protein} \\
\text{First generation} & DNA \arrow[r, "A"] \arrow[d, "R"] & RNA \arrow[r, "B"] & \text{protein} \\
\text{Second generation} & DNA \arrow[r, "A"] & RNA \arrow[r, "B"] & \text{protein}
\end{tikzcd}$$

The step A is called transcription step; step B, translation step and step R, self-replication step.

The synthesis of proteins is different in at least one basic respect from the manufacture of other cellular compounds like glycogen, starch or lipids. A glycogen molecule, for example, is composed of identical glucose units and is structured like any other glycogen molecule containing the same number of glucose units. On the other hand, an organism, makes its own *specific* proteins and no two individuals have identical proteins. For only if newly formed proteins are exactly like those present earlier can a cell maintain its own special characteristics. Since a protein molecule is composed of *different* kinds of amino acid units, a random linking together of such units would make one polypeptide chain quite different from every other. Protein synthesis therefore requires *specificity control*, in other words, a "*blue print*" must provide instructions about the precise sequence in which given numbers and types of amino acids are to be joined as a protein. Ultimately, this specificity control is exercised by the genes of a cell, that is the DNA of the chromosomes. (The chromosomes are thread-like structures present in the, nucleus of a cell on which genes are arranged in a specific sequence. A gene is a segment of DNA molecule which codes or specifies for one polypeptide chain. The number of chromosomes per cell per species is constant; man has 46 and potato has 40 chromosomes per cell). *The primary function of genes is to control specificities in protein synthesis.*

20.14 BIOLOGICAL ASPECTS OF AGEING

It is common observation among humans and other living organisms that they grow old in course of time. During the aging process, the human body as a whole experiences loss of coordination and working capacity. Besides, the skin gets wrinkled and hardened. It always was and is still intriguing to the man to find out the causes of getting old. Only recently, scientists have started investigating whether there is any method of slowing down the ageing process.

Now a days, the ageing process is being studied at the level of body cells One extreme theory, suggests that DNA of each cell carries its own programme for self destruction. Another view is that the cells age and die as a result of environmental causes such as exposure of DNA to radiations of various types. The damage of DNA eventually leads to destruction of the cells.

With ageing, the cells accumulate 'waste' materials either inside or around them. These could possibly obstruct their normal activity.

There is no sufficient data for or against any of these theories.

Another theory for the cause of cellular damage and ageing concerns the lysosomes contained within the cells. The lysosomes are small bag of enzymes concerned with the digestion of materials brought into the cell from outside. The lysosomal enzymes have very powerful degradative action on any biological material with which they come into contact. The reason they do not break down the cell substances is that they are enclosed within a membrane and do not normally come into contact with the cell constituents. This theory states that sometimes the bag may break and cause the enzymes to escape. In such a situation cellular damage can occur.

Lysosomal theory is the modern one and the discoverer of lysosome got nobel prize

EXERCISES

20.1 Why do living organisms need energy to keep them living ? How do they acquire this energy ?

20.2 What role is played by chlorophyll in the functioning of plants ?

20.3 Why are naturally occurring amino acids and sugars optically active ? What type of activity is generally shown by them ?

20.4 Define and illustrate the following :

(a) carbohydrates, (b) amino acids, (c) denaturation, (d) DNA,
(e) fat, (f) oil, (g) furanose, (h) lipids,
(i) monosaccharides, (j) nucleotide, (k) pyranose, (l) RNA.

20.5 What are the hydrolysis products of cane sugar, and milksugar, starch.

20.6 Write structural formulae for tristearin and triolein which are stearic acid and oleic acid esters of glycerol.

20.7 State the reactions in which following enzymes will function :

(a) lipase (b) amylase (c) cellulase (d) invertase.

20.8 Why does heating cause loss of activity of enzymes ?

20.9 What is the difference between :

(a) RNA and DNA (b) nucleoside and nucleotide (c) ribose and deoxyribose.

20.10 Describe a simple test to find out whether a fat has unsaturated acid or not.

UNIT 21

Chemistry in the Service of Man

Chemists have not only developed more economical and convenient methods of recovering useful materials from nature but have also made many new substances used by man to improve his living conditions These include various medicinal compounds, agricultural chemicals and polymers used as substitutes for fibres and structural materials like stones wood and metals. Soaps and synthetic detergents are now common household articles. In this Unit we shall describe some of the more important of such substances

21.1 POLYMERS

There are two kinds of polymers: *natural polymers* such as cellulose, wood, silk, skin, rubber, and *synthetic polymers* such as synthetic rubber, synthetic textile fibres (terylene, polyester, etc.) and various plastic materials used in the manufacture of products ranging from baby bottles to automobile bodies. The synthetic polymers, as the name implies, are made from some ordinary simple chemical substances.

21.1-1 NATURAL POLYMERS

Amongst natural polymers, cellulose and its derivatives are industrially most important. Whereas wool, silk, and leather are proteins and natural rubber is a polymer of the hydrocarbon isoprene, cellulose obtained from cotton and wood is a polysaccharide consisting of cellobiose units, About 60% of wood and 90% of cotton is cellulose. After removing the impurities such as waxes, fats and pectin like substances, purified cellulose may be used as such or it may be used for the manufacture of rayon, cellulose acetate fibres, cellophane, explosives like "gun cotton" and plastics like celluloid.

Cellulose is not a single chemical. It consists of at least two main parts, α-and β-cellulose. Whereas β-cellulose dissolves in 17-18% aqueous solution of sodium hydroxide, α–cellulose does not do so. Rayon and cellophane are made from α–cellulose by the *viscose process.* A suspension of α–cellulose in sodium hydroxide is allowed to react with carbon disulphide. The product is obtained in the form of a viscous syrupy solution known as *viscose.*

$$\alpha\text{–Cellulose} + NaOH + CS_2 \longrightarrow \text{Viscose}$$

When viscose is extruded through narrow pin holes or slits into a solution of sulphuric acid, the cellulose can be reprecipitated as a continuous rayon filament or as cellophane sheets.

$$\text{Viscose} + H_2SO_4 \longrightarrow \text{Cellulose as rayon or cellophane} + CS_2 + NaHSO_4$$

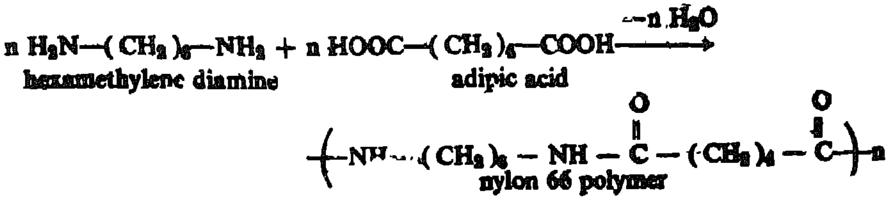
Esters and ethers of cellulose are also widely used in industry. Among the esters, nitrate, acetate, and butyrate are important. Cellulose mono-and di-nitrates are used in the celluloid industry after mixing with camphor, castor oil and other plasticizing agents Nitrated cellulose, containing more than 13% *N*, is explosive and is called "gun cotton".

21.1-2 SYNTHETIC POLYMERS

Synthetic polymers are made in factories from substances with small molecules called monomers. Two types of polymerization processes are used: *addition polymerization*, in which the monomer molecules simply add together to form chains and *condensation polymerization* in which new bonds are formed by elimination of small molecules like H_2O. Addition polymerization is induced by ions or free radicals. Thus in the polymerization of vinyl chloride ($CH_2{=}CHCl$), the free radicals help in opening up the double bond of the monomer and to initiate the polymerization reaction:

$$\underset{\substack{\text{free}\\\text{radical}}}{R^{\cdot}} + \underset{\substack{\text{vinyl}\\\text{chloride}}}{CH_2{=}CHCl} \longrightarrow R{-}CH_2{-}CHCl \longrightarrow R(CH_2{-}CHCl)_n$$

This process stops when another free radical gets attached to the other end of the chain. The manufacture of nylon 66 involves condensation copolymerization of hexamethylene-diamine and adipic acid. Each of these monomers contain 6 carbon atoms.



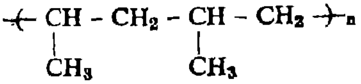
$$\underset{\text{hexamethylene diamine}}{n\,H_2N{-}(CH_2)_6{-}NH_2} + \underset{\text{adipic acid}}{n\,HOOC{-}(CH_2)_4{-}COOH} \xrightarrow{-n\,H_2O} \underset{\text{nylon 66 polymer}}{\left(NH{-}(CH_2)_6{-}NH{-}\overset{\overset{O}{\|}}{C}{-}(CH_2)_4{-}\overset{\overset{O}{\|}}{C}\right)_n}$$

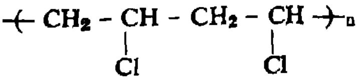
The polymerization reaction continues till all of one or the other reactant is used up.

21.1-3 ADDITION POLYMERS

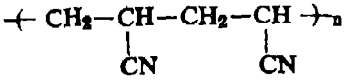
These include the diene polymers in general such as polyethylene or polythene, polyvinyl chloride (PVC), polystyrene, etc

Polyethylene or polythene, $-\!\!\left(-CH_2-CH_2-CH_2-CH_2-\right)\!\!-_n$: This polymer is made of ethylene and is used as films, sheets and as coatings for electric wires, cables and other materials. It is also used in the manufacture of polythene pipes, bottles, buckets, etc.

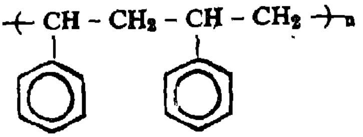
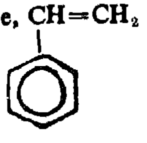
Polypropylene,  $-\!\!\left(\underset{\substack{|\\ CH_3}}{CH}-CH_2-\underset{\substack{|\\ CH_3}}{CH}-CH_2\right)\!\!-_n$ is harder and more tenacious than polythene. It is obtained from propylene and is used for ropes, fibres, seat covers, etc. and in the manufacture of stronger pipes and bottles.

Polyvinylchoride (PVC),  $-\!\!\left(CH_2-\underset{\substack{|\\ Cl}}{CH}-CH_2-\underset{\substack{|\\ Cl}}{CH}\right)\!\!-_n$

It is a pliable polymer made from vinyl chloride ($CH_2=CHCl$) and has very wide applications. It is used in the manufacture of raincoats, hand bags, plastic dolls, curtain cloths and vinyl flooring. It is a good electrical insulator and is used for wires, cables and other electrical goods PVC is also used in making gramophone records and hose pipes.

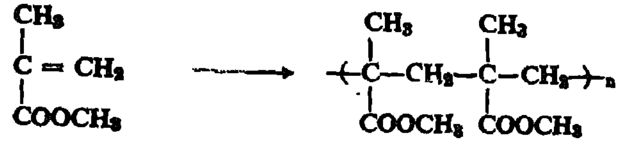
Polyacrylonitrile,  $-\!\!\left(CH_2-\underset{\substack{|\\ CN}}{CH}-CH_2-\underset{\substack{|\\ CN}}{CH}\right)\!\!-_n$

It is a polymer of acrylonitrile ($CH_2=CHCN$) and is used for the manufacture of Orlon and Acrilan fibres.

Polystrene,  is the polymer of styrene, 

It is a good transparent polymer and is used in the fabrication of plastic toys, household wares, radio and television bodies, refrigerator linings, etc.

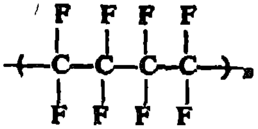
Polymethylmethacrylate (PMMA) is a polymer of methylmethacrylate. It can take up beautiful colours and tints and is widely used in the manufacture of lenses, light covers, lamp shades, plastic jewellary, signboards, moulded novelties dentures skylights and for decorative purposes in buildings. Its outstanding property is its clearness and excellent light transmission (even better than glass). Its commercial names are Lucite, Plexiglass, Acrylite and Perspex.



$$\underset{\text{methylmethacrylate}}{\overset{\displaystyle CH_3}{\underset{\displaystyle COOCH_3}{\overset{|}{\underset{|}{C}}}}=CH_2} \longrightarrow \underset{\text{polymethylmethacrylate}}{-\!\!\left(\overset{CH_3}{\underset{COOCH_3}{C}}-CH_2-\overset{CH_3}{\underset{COOCH_3}{C}}-CH_2\right)\!\!-_n}$$

methylmethacrylate polymethylmethacrylate

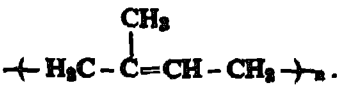
Polytetrafluoroethylene (Teflon) is a polymer of tetrafloroethylene, $CF_2=CF_2$ and has the structure;



$$-\!\!\left(\overset{F}{\underset{F}{C}}-\overset{F}{\underset{F}{C}}-\overset{F}{\underset{F}{C}}-\overset{F}{\underset{F}{C}}\right)\!\!-_n$$

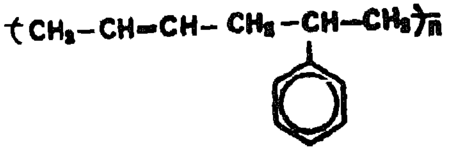
It is quite flexible and chemically very inert. It is used for making gaskets, pump packings, valve seals, non-lubricated bearings, filter cloths, etc., where high resistance to chemicals and heat is required.

Synthetic rubbers : Natural rubber, which is obtained from the latex of the rubber trees, is a linear polymer of isoprene, ($CH_2=\underset{CH_3}{C}-CH=CH_2$) and may be represented as



$$-\!\!\left(H_2C-\overset{CH_3}{C}=CH-CH_2\right)\!\!-_n.$$

Synthetic rubbers are not identical with natural rubber but resemble it in many properties. Thus a copolymer of butadiene and styrene, Buna-S (Bu for butadiene, na the symbol for sodium, Na, which is polymerizing agent and S for styrene) is used for automobile tyres.



Buna-S

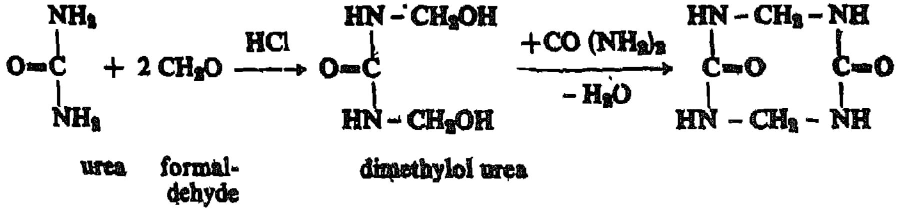
Neoprene is a polymer of chloroprene ($H_2C{=}\underset{\underset{Cl}{|}}{C}-CH{=}CH_2$). This is also an excellent rubber-like material.

There are other innumerable addition polymers in the market such as polyvinylacetate polymer used in paints and copolymer of vinylacetate for floor coverings, upholstering materials, flexible sheetings, films, etc.

21.1-4 CONDENSATION POLYMERS

As mentioned earlier, these are made by condensation reactions involving loss of a small molecule such as water, methanol or hydrogen halide between condensing units. Some of such polymers are resins like urea-formaldehyde, phenol-formaldehyde (Bakelite) and glyptal and fibres like terylene and nylon.

Urea-formaldehyde resins: These are made by the condensation of urea and formaldehyde under acidic conditions.

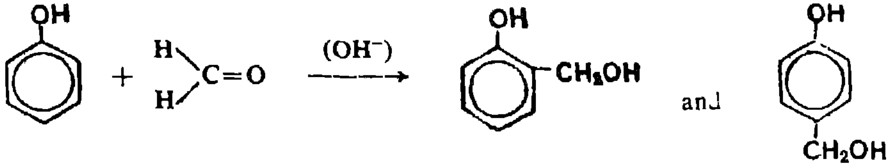


$$\begin{array}{c}NH_2\\|\\O{=}C\\|\\NH_2\end{array} + 2\,CH_2O \xrightarrow{HCl} \begin{array}{c}HN-CH_2OH\\|\\O{=}C\\|\\HN-CH_2OH\end{array} \xrightarrow[-H_2O]{+CO(NH_2)_2} \begin{array}{ccc}HN-CH_2-NH\\|\qquad\qquad|\\C{=}O\qquad C{=}O\\|\qquad\qquad|\\HN-CH_2-NH\end{array}$$

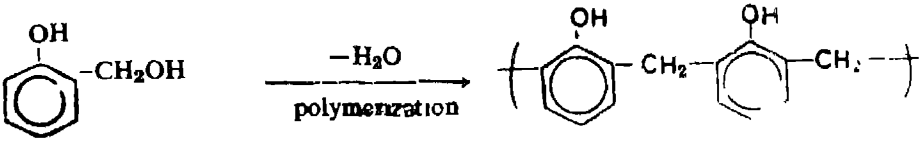
The unpolymerized resins are colourless, water-soluble materials extensively used in the bonding of sheets of paper, cloth or wood such as plywood. The polymerized resins are chemically inert, resistant to solvents, have a hard, durable surface and are thermosetting. They cannot be reshaped by heating.

Phenol-formaldehyde resins (Bakelite): They are made by the reaction of phenol and formaldehyde in the presence of a basic catalyst. The reactions involve formation of methylene bridges in *ortho*, *para* or both *ortho* and *para* positions

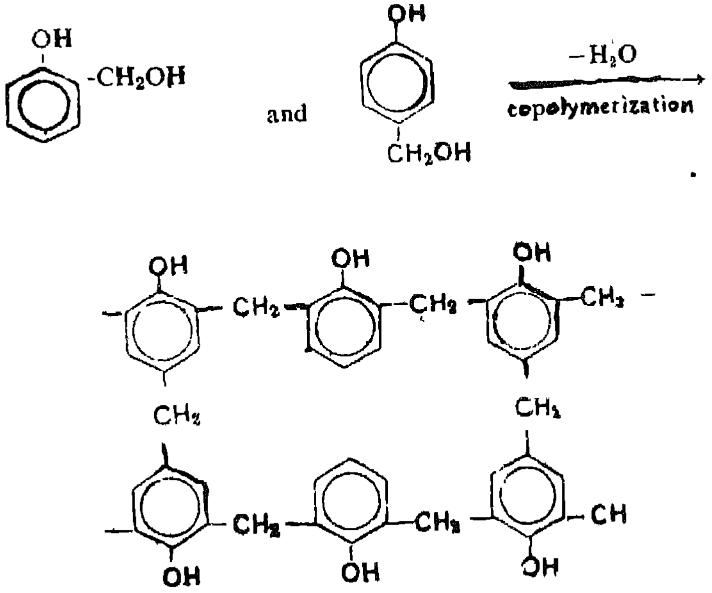
Thus linear or crosslinked materials can be prepared.



intermediate *ortho*-and *para*-hydroxyl methyl phenols



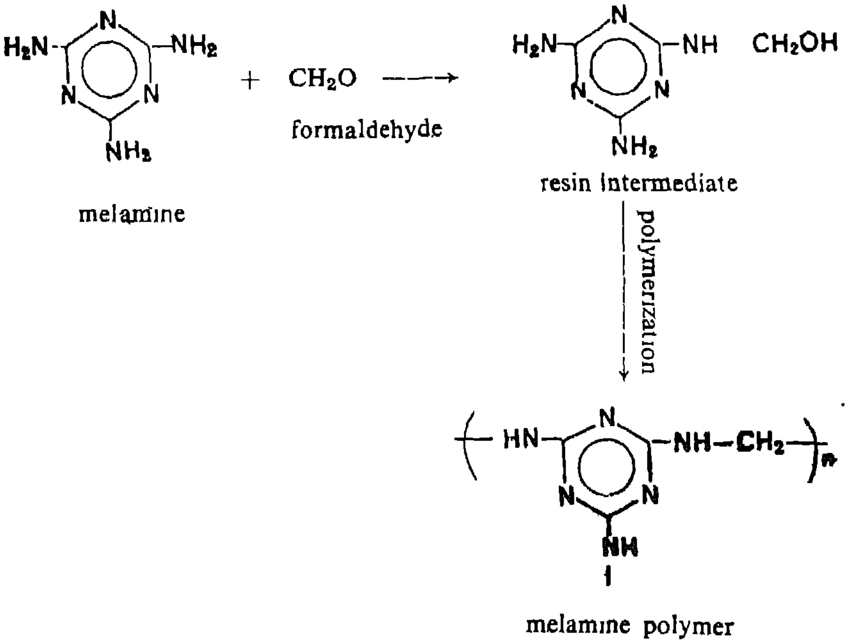
linear polymer



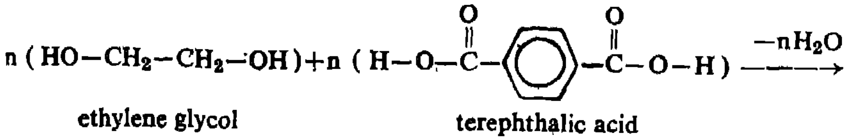
crosslinked polymer-Bakelite

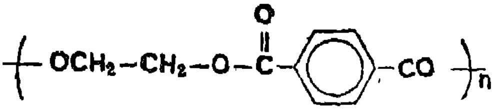
Crosslinked bakelite is a thermosetting polymer. Soft bakelites with low degree of polymerization are used as bonding glue for laminated wooden planks and in varnishes and lacquers. High degree of polymerization leads to formation of hard bakelites which are used for making combs, fountainpen barrels, phonograph records, electrical goods, formica table tops and many other products. Sulphonated bakelites are used as ion-exchange resins.

Melamine and *formaldehyde* copolymerize to give another polymer used in making plastic crockery Cups and plates made from melamine polymer are hard and do not break on being dropped



Terylene or Dacron: The polyester of terephthalic acid and ethylene glycol, when made into textile fibres is called Terylene or Decron. It is highly crease-resistant, durable and is not damaged by pests like moths and mildew.

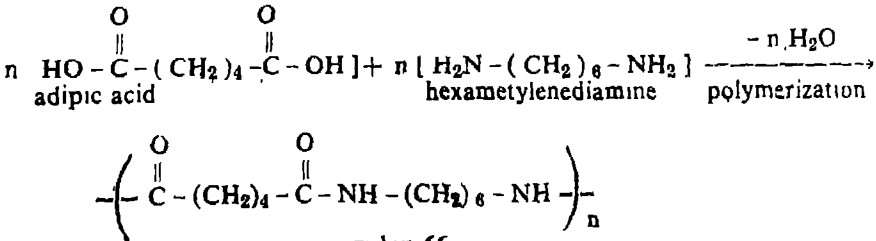




dacron or terylene

Nylon : The name 'Nylon' has been applied to a polyamide which is usually made from dibasic acids and diamines.

For example, Nylon-66 is a polyamide formed by the reaction of the adipic acid and the hexamethylenediamine Several other varieties of nylon have now been made



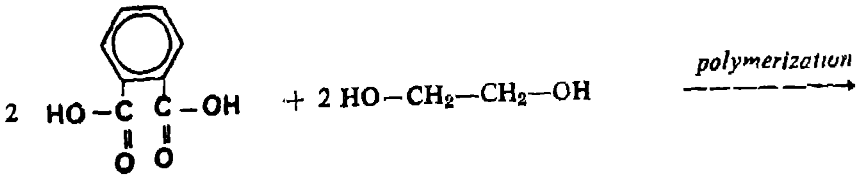
$$n\ \underset{\text{adipic acid}}{HO-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-OH\,]} + n\,\underset{\text{hexametylenediamine}}{[\,H_2N-(CH_2)_6-NH_2\,]} \xrightarrow[\text{polymerization}]{-n\,H_2O}$$

$$-\left(-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-NH-(CH_2)_6-NH-\right)_n-$$

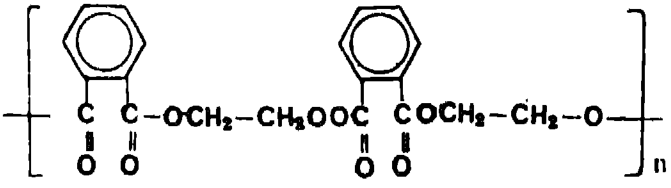
nylon-66

Nylon is usually fabricated into sheets, bristles for brushes and textile fibres It has high tensile strength and good elastic recovery. Crinkled nylon fibre is used for making elastic hosiery.

Glyptal or alkyd resins . These are polyesters of polybasic carboxyl acids, and polyhydric alcohols, for example, phthalic acid and ethylene glycol. These are thermoplastic in nature They are used mainly in the manufacture of paints and lacquers

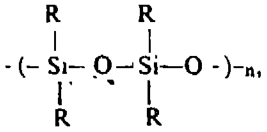


phthalic acid ethylene glycol



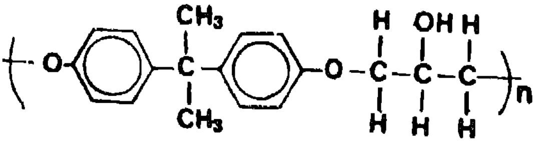
glyptal

Amongst other polymers available in the market are epoxy resins and silicone polymers. Epoxy resins stick to smooth surfaces and act as good binders. Silicones are elastic polymers which are used as protective coatings and as high temperature lubricants



$$-(-\underset{R}{\overset{R}{Si}}-O-\underset{R}{\overset{R}{Si}}-O-)-_n$$

silicone



epoxy resin

21. 2 CHEMICALS IN AGRICULTURE

There are two major uses of chemicals in agriculture. One is as chemical fertilizers and the other, as pesticides. Pesticides are materials used for kiling pests harmful for crops.

21.2-1 FERTILIZERS

There are three main types of chemical fertilizers :

(1) *Nitrogenous fertilizers :* Examples of these are ammonia, ammonium sulphate, ammonium nitrate, calcium ammonium nitrate (CAN), and urea [$CO(NH_2)_2$]. All these provide nitrogen in the form of ammonia, either directly or due to alkalinety of soil. The nitrates are reduced to ammonia by soil bacteria. CAN is a popular fertilizer. It is a stable, safe and non-hygroscopic substance It can be easily stored. Another popular nitrogenous fertilizer is urea. It has all the good points of CAN and in addition, it has a higher percentage of nitrogen. Calcium cyanamide ($CaNCN$) is a nitrogenous fertilizer which slowly forms ammonia by reaction with soil moisture.

$$CaNCN + 3H_2O \longrightarrow CaCO_3 + 2NH_3$$

Urea	$CO(NH_2)_2$	46.67% nitrogen
CAN	$Ca(NO_3)_2 . NH_4NO_3$	22.95% nitrogen
Calcium cyanamide	$CaNCN$	50.00% nitrogen

(2) *Phosphate fertilizers* : Soil provides phosphorus to the plants in the form of water soluble phosphate. The cheapest sources of phosphorus are the mineral phosphorite and bone ash. Both of these consist of insoluble calcium phosphate [$Ca_3(PO_4)_2$].

Due to alkaline nature of most soils, calcium phosphate remains insoluble. However, if calcium phosphate be treated with adequate mineral acids, it can be converted to the water soluble calcium dihydrogen phosphate [$Ca(H_2PO_4)_2$].

$$Ca_3(PO_4)_2 + 4\ H^+ \longrightarrow Ca(H_2PO_4)_2 + 2\ Ca^{2+}$$

If a calculated quantity of sulphuric acid be used as a source of hydrogen ions, the calcium ions are fixed as $CaSO_4$.

$$Ca_3(PO_4)_2 + 2\ H_2SO_4 \longrightarrow Ca(H_2PO_4)_2 + 2\ CaSO_4$$

This is a very important use of sulphuric acid. The mixture of calcium sulphate and calcium dihydrogen phosphate thus obtained is commercially known as *superphosphate*. If phosphoric acid be used, we get a product consisting of only calcium dihydrogen phosphate.

$$Ca_3(PO_4)_2 + 4\ H_3PO_4 \longrightarrow 3\ Ca(H_2PO_4)_2$$

This product is known as *triple superphosphate*. It has the advantage of being free from inert material like calcium sulphate. There is a considerable saving on transport of the fertilizer. Due to the alkaline nature of soil, superphosphate is soon converted to the insoluble form.

The strength of a phosphatic fertilizer is determined on the basis of percentage of P_2O_5 in it.

Superphosphate	$Ca(H_2PO_4)_2 . 2CaSO_4$.	20.8% P_2O_5
Triple superphosphate	$Ca(H_2PO_4)_2$	65.0% P_2O_5

(3) *Potash fertilizers* : Plants need soluble potassium salts for their proper development. In nature this potassium comes from the weathering of rocks.

However, for intensive cultivations, potassium compounds are added to the soil Most common compound used to provide soluble potassium to plants is potassium chloride It is sold under the name of *muriate of potash* However, for tobacco crop potassium sulphate is preferred to potassium chloride. The use of latter compound yields tobacco, which gives easily fusible ash. This makes it unfit for use in cigarettes. The ash of tobacco grown with potassium sulphate as fertilizer is high melting

Potassium nitrate can also be used as fertilizer.

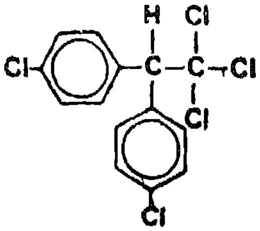
Our sources of potash and phosphorus are rather limited and these need to be conserved for use as fertilizers

21.2-2 PESTICIDES

Pests are animals and plants detrimental to the interest of man. Micro-organisms and viruses causing infectious diseases are, however, arbitrarily excluded. Rodents, insects and weeds of several kinds play a havoc with our economy and need a careful control. The chemicals used for destruction of insects in particular are called *insecticides* These and others used for destroying rodents (rodenticides), mites (miticides), nematodes (nematocides), fungi (fungicides) and weeds (herbicides) are together called *pesticides*

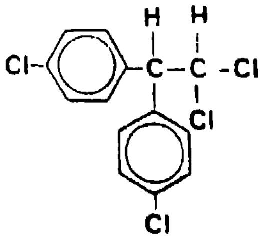
Most common pesticide is DDT. These letters stand for *d*ichloro*d*iphenyl*t*richloroethane A more apt name for it is 2, 2-bis (*p*-dichlorophenyl)-1, 1', 1-trichloroethane DDT is an example of chlorinated hydrocarbons used for destruction of insects.

Several others similar to and different from DDT have been synthesized and are in use.

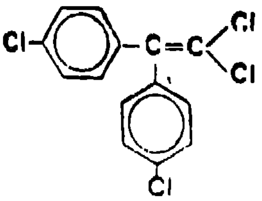


DDT

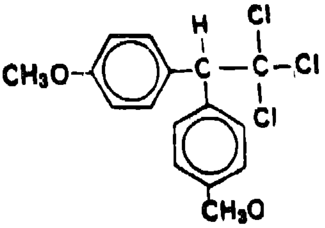
Formulae of some of these are shown here.



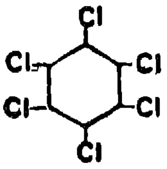
DDD



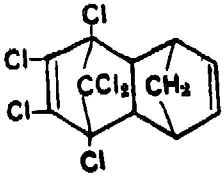
DDE



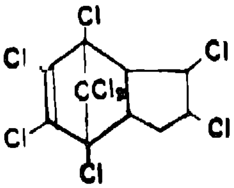
methoxychlor



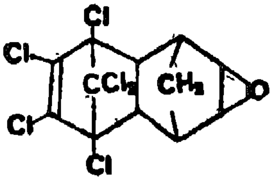
benzene hexachloride (BHC) or lindane, $C_6H_6Cl_6$



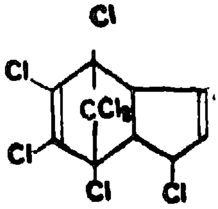
aldrin
$C_{12}H_8Cl_6$



chlordane
$C_{10}H_6Cl_8$



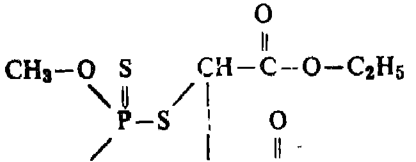
dieldrin
$C_{12}H_8Cl_6O$



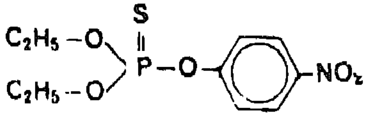
heptachlor
$C_{10}H_5Cl_7$

The use of these insecticides has resulted in side problems of development of resistence in insects and malfunctioning in birds and fishes due to their accumulation in animal bodies. DDT is still much in use inspite of its harmful effects because of non-availability of cheaper insecticides. Gammexane or 666 known in trade as hexachlorobenzene is wrongly named. It is in fact a stereoisomer of benzene-hexachloride.

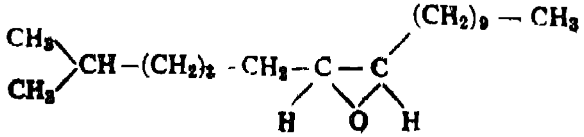
A second large group of insecticides is represented by organo-phosphates. They have the advantage of easier degradation and are therefore less persistent in action. Their chemical structures are similar to nerve gases used in chemical warfare. Malathion and parathion are examples of this group of insecticides. Malathion is relatively safer but all insecticides of this group are highly toxic to man and domestic animals Due to their lesser stability, they have to be applied more often The insecticides are fairly general in action and destroy the useful along with the harmful insects. Another novel chemical method of insect control is by using sex-attractants. These chemicals are naturally exuded by some female insects to attract their males and are effective in very small concentrations. They are very specific in action. One example of such chemicals is *disparlure*. It has been used against gypsy moth



malathion

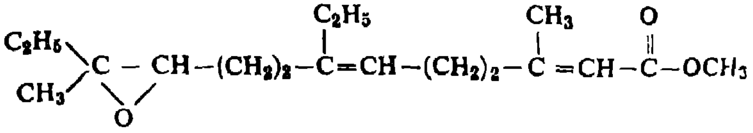


parathion



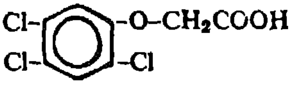
disparlure

Such substances are given the group name *pheromones* Ants use some such substance to lay a track for their group movements A more recent attempt to control insects is to use hormones for upsetting the growth cycles One such substance is *cecropia moth juvenile hormone* Its structure is

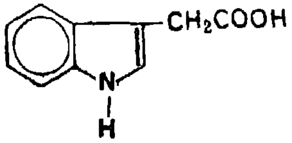


cecropia moth juvenile hormone

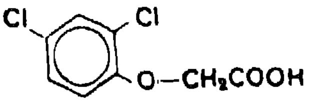
Herbicides are a group of chemicals used for killing weeds. A group of herbicides is chemically similar to the natural plant hormone indole acetic acid These stimulate the growth of broad-leafed plants to the destruction point. An example of such substance is 2,4-D (2,4-dichlorophenoxyacetic acid) and another is 2,4,5-T (2,4,5-trichlorophenoxyacetic acid).



2, 4, 5-T

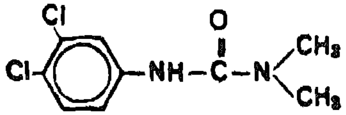


indole acetic acid



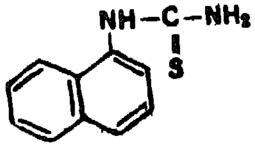
2,4–D

Some herbicides act by inhibiting photosynthesis of glucose in certain plants. Diuron belongs to this group.



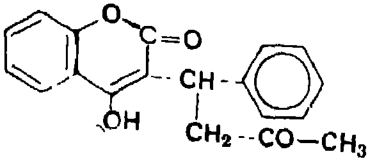
diuron

Rats (rodents) not only destroy stocks of food, they also spread diseases. They are destroyed by using sodium monochloroacetate, sodium fluoroacetate, zinc phosphide, or thalium sulphate mixed with food. Alpha-naphthylthiourea (ANTU) is an organic chemical used for killing rodents



ANTU

Warfarin discovered by Wisconsion Alumni Research Foundation (hence the name) has been found to be more useful as it is much less toxic to other animals. Chemically, it is 3-(α-acetonyl benzyl)-4-hydroxy coumarin.



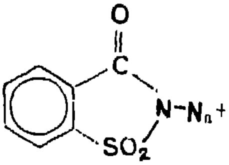
warfarin

Amongst fungicides we have copper naphthenate, copper sulphate, 2,4,5-trichlorophenol and some mercury compounds. Bordeaux mixture consists of copper sulphate, lime and water.

For preservation of underground portions of woods phenols of coal tar (creasote oil) are used.

21.3 FOOD ADDITIVES

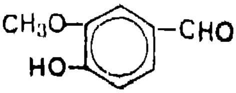
All those materials which are added to food to improve its appearance, taste, odour, food value and for keeping properties, and are permitted by law are called *food additives* A variety of food colours are currently in use but it is suspected that some of these can cause cancer. This practice should be discouraged. For improving taste and odour spices are added. Most important chemicals to be added for taste are the synthetic sweetening agents Most important of these and perhaps the only safe one is saccharin which is used as its soluble sodium or calcium salt



sodium salt of saccharin

It is about 600 times sweeter than sugar.

Vanillin, an aromatic aldehyde is used for vanila flavour in custards, cakes, icecream, etc.

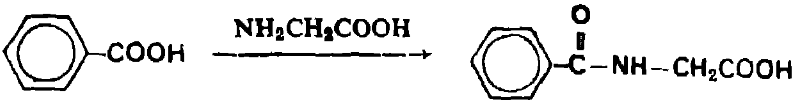


vanillin

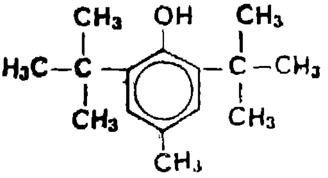
Salts and vitamins may be added to food to replace the minerals and vitamins lost in food processing Food preservatives include substances which prevent oxidation processes and bacterial actions or both A common preservative for squashes and acid foods like pickles is potassium or sodium *metabisulphite*,

$$(Na_2S_2O_5 \equiv Na_2SO_3 + SO_2)$$

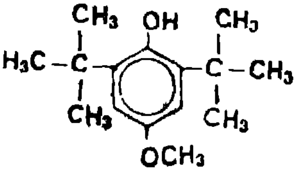
It is a reducing agent, as well as a germicide Benzoic acid (C_6H_5COOH) is used in various foods as such or as its sodium salts. It retards bacterial growth and is metabolized to hippuric acid which is excreted in urine.



Amongst antioxidants in use are **butylated hydroxy toluene (BHT) and butylated hydroxy anisole (BHA).**



BHT



BHA

Antioxidants prevent ageing of food materials

21.4 SOAPS AND DETERGENTS

The characteristic feature of soaps and detergents is that they tend to concentrate at the surface of the solution or interfaces. Their solutions form coherent films. This property enables them to reduce surface tensions of solution and to cause foaming. They can emulsify greases and remove dirt and dust. Such substances are said to be *surface active agent* or *surfactants*. The molecule of a surface active substance contains two characteristic groups, a water-soluble (hydrophilic) group and an oil-soluble (lipophilic)* group Thus one end of the molecule tends to go into the oil phase and the other end tends to go into the water phase, with the net result that the material concentrates at the interface.

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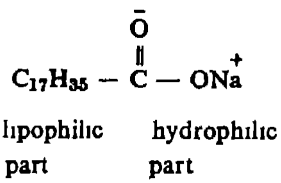
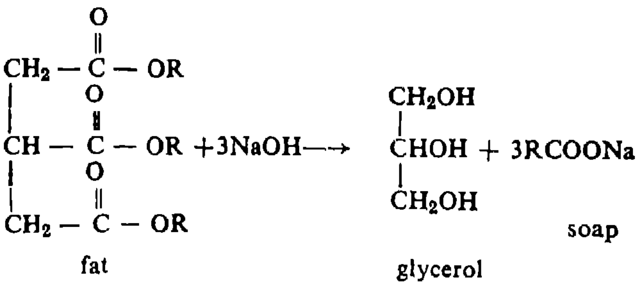
* The word lipophilic comes from "lipids" which stands for oils in general.



$$C_{17}H_{35}-\overset{\overset{\bar{O}}{\|}}{C}-O\overset{+}{Na}$$

Soap. Ordinary soap is a sodium or potassium salt of a fatty acid such as lauric ($C_{11}H_{23}COOH$), myristic ($C_{13}H_{27}COOH$), palmitic ($C_{15}H_{31}COOH$), stearic ($C_{17}H_{35}$ $COOH$), oleic ($C_{17}H_{33}COOH$) or linoleic ($C_{17}H_{31}COOH$) acids The fatty acids are obtained by the hydrolysis (saponification) of fats and oils



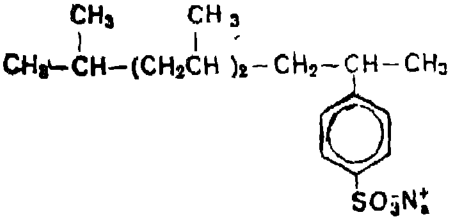
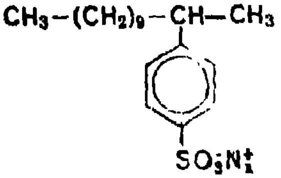
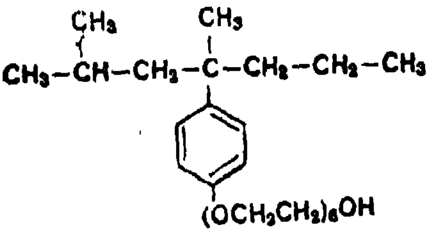
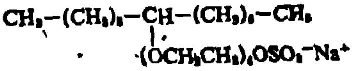
Soap is an excellent detergent and has 100 per cent biodegradability Micro-organisms present in sewage can completely oxidize soap to CO_2 and no pollution problems arise from used soaps But soaps have two disadvantages : firstly, they form insoluble substances when *hard water* is used

The calcium and the magnesium ions present in hard water form insoluble calcium and magnesium soaps Secondly, from an industrial standpoint, soaps cannot be used in acidic solutions since acids precipitate the insoluble free fatty acids. These fatty acids may adhere to the fabrics during processing, and prevent the even application of dyestuffs.

Synthetic Detergents. Most of the commercial detergents have C_8 to C_{22} hydrocarbon lipophilic groups and any one of the following four hydrophilic groups : (1) Anionic groups such as the sulphonate, sulphate or carboxyl group These are commercially more important. (2) Cationic groups such as amine salts or quaternary ammonium compounds (3) Amphoteric groups containing both anionic and cationic parts, commercially these are relatively unimportant. (4) The non-ionic type groups such as alcohols, and ethers. Some examples of typical detergents are given in Table 21.1.

TABLE 21.1

Some Detergents

Detergent	*Class*	*Biodegradability*	*Typical Formula*
Soap	anionic	100%	$C_{17}H_{35}COO^-Na^+$
Alkylbenzene sulphonate (ABS)	anionic	50-60%	
Linear alkylbenzene sulphonate (LAS)	anionic	90%	
Lauryl alcohol, sulphated	anionic	100%	$CH_3-(CH_2)_{11}-O-SO_3^-Na^+$
Nonylphenol, ethoxylated	nonionic	30%	
Secondary alcohol, ethoxylated and sulphated	anionic	100%	 $\underset{(OCH_2CH_2)_6OSO_3^-Na^+}{CH_3-(CH_2)_8-CH-(CH_2)_6-CH_3}$

The most widely used domestic detergent is the linear alkylbenzene sulphonate (LAS) also called sodium dodecylbenzene sulphonate (SDS) The sulphated and sulphonated detergents do not form precipitates with calcium and magnesium ions present in hard water as the calcium and magnesium alkyl sulphates or sulphonates are soluble in water Secondly, these can be used in acidic conditions also

The detergents are now a days very commonly used in washing machines for clothes and crockery

21.5 CHEMICALS IN MEDICINES

Substances used for treatment of diseases and for reducing suffering from pain are called medicines or drugs All such drugs are either single chemicals or their mixtures. Medicines act in serveral different ways. A description of these is beyond the scope of present text book Here we shall learn about the general effects of medicines and some of their common examples. Medicines should be taken under proper medical advice and they are prone to have side effects and can produce different and more intense effect and sometimes permanent damages to our bodies if they are taken in excessive dozes or for too long intervals.

21.5-1 ANTISEPTICS, DISINFECTANTS AND GERMICIDES

Antiseptics prevent growth of micro-organisms or may even kill them but are safe to be applied to living human tissues. They can be applied to wounds, ulcers and diseased skin surfaces

Disinfectants kill micro-organisms but they are not safe for contact with living tissues. They are applied to inanimate objects like instruments, floors, drains and public bath rooms.

Germicide is a general term applicable to all substances which can kill or destroy various germs, fungi and viruses.

The same substance can act as antiseptics as well as disinfectants according to the concentration of the solution used. Thus, a 0.2% solution of phenol in water is an antiseptic, a 1% solution is a disinfectant and a 1 3% solution is a fungicide.

Chlorine is used for making water fit for drinking at a concentration of 0 2 to 0.4 parts per million (ppm). Low concentrations of sulphur dioxide are used for sterilizing squashes for preservation. The same gases are used as disinfecants for living rooms when infected with disease germs and bacteria

Most of the chemicals used as antiseptics, disinfectants and germicides are metabolic poisons or strong oxidizing agents for organic matter Common examples are listed in Table 21.2

TABLE 21.2

Antiseptics, Disinfectants and Germicides

Poisons.

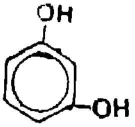
Mercuric chloride or bichloride of mercury ($HgCl_2$), 0 1% solution

Mercurochrome (a red coloured organic mercurry compound)

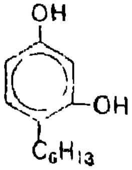
Formaldehyde

Phenol and cresols, salicylic acid, picric acid

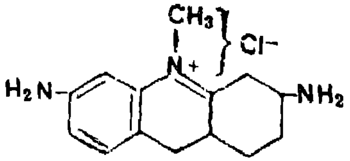
Resorcinol,



5 hexyl resorcinol,



Acriflavine (a yellow dye),



Silver nitrate and colloidal silver

Boric acid (a mild antiseptic)

DDT

Oxidizing agents :

Potassium permanganate solutions (up to 1%)

Solutions of chlorine, sodium hypochlorite (NaOCl, Dakin solution)

Bleaching powder, tincture of iodine, iodoform

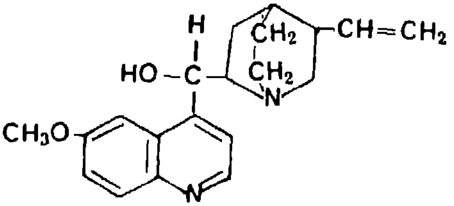
Hydrogen peroxide (3% solution)

Alkalies :

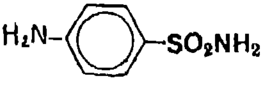
Caustic soda and polyphosphate

21 5-2 CHEMOTHERAPY

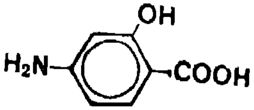
It is a method of curing a disease by using some specific chemicals against the disease causing micro-organisms. Some important examples of chemotherapeutic drugs are quinine and chloroquine phosphate for malaria, emetine against amaeba and piperazine against round worms and pin worms. Sulphanilamide and other allied sulpha-drugs like sulphadiazine, are chemotherapeutic agents used for bronchitis, sore throat infections and boils PAS (*para*-aminosalicylic acid and INH (*iso*-nicotin-hydrazine or isoniazid) are chemotherapeutic remedies for tuberculosis.



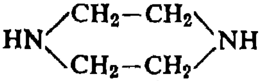
quinine



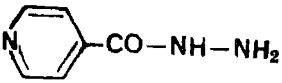
sulphanilamide



PAS (*para*-amino salicylic acid)



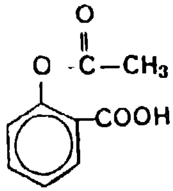
piperazine



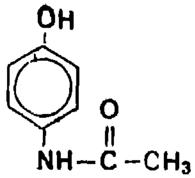
INH (*iso*-nicotin hydrazine, isoniazid)

21.5-3 ANTIPYRETICS

These substances are used to bring down temperature in high fevers. Their administration often leads to perspiration. Common examples are aspirin (acetyl salicylic acid), phenacetin, paracetamol (4-acetamidophenol) and novalgin (analgin). Quinine also has some antipyretic effect. Most common antipyretics in use has been aspirin but because of the salicylic acid generated by it in the stomach, it can ulcerate stomach wall and can cause bleeding there from. It should not be taken on empty stomach or indiscriminately. Calcium and sodium salts of aspirin are more soluble and less harmful.



acetylsalicylic acid
(aspirin)



4-acetamidophenol
(*para*-acetamol)

21.5-4 ANALGESICS

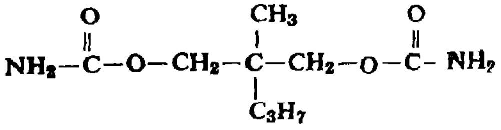
These are the drugs used for relieving pain. Aspirin and some of the other antipyretics act as analgesics also.

Narcotics : These are the drugs which produce sleep and unconsciousness, if taken in higher doses. Drugs of this group are also used as very effective analgesics

Typical examples are the alkaloids* of opium, namely morphine, codein and heroin. They have complex structures. They are known to be habit forming, and to guard against addiction and misuse They are not sold without proper medical prescription.

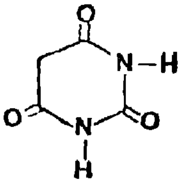
21.5-5 TRANQUILIZER AND HYPNOTICS

These drugs act on higher centres in the central nervous system and help in reducing anxiety. They are constituents of sleeping pills. Their misuse and use without adequate reasons is frequent. They can be habit forming and should not be taken without consulting a doctor. Some of these like luminal and seconal are derivatives of barbituric acid. Equanil (meprobamate) is a different type

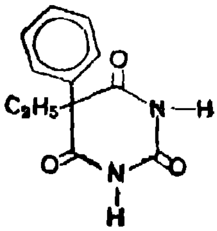


$$NH_2-\overset{\overset{O}{\|}}{C}-O-CH_2-\underset{\underset{C_3H_7}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-O-\overset{\overset{O}{\|}}{C}-NH_2$$

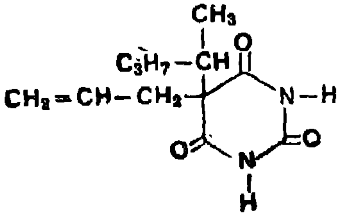
equanil



barbituric acid



luminal



seconal

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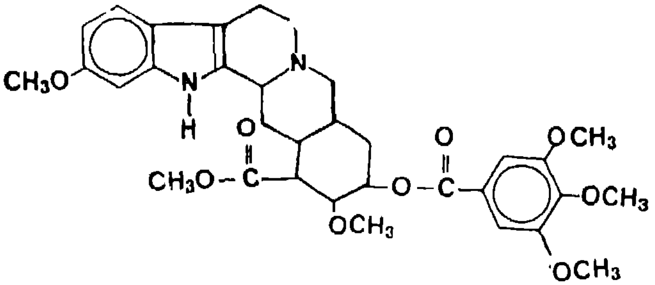
*Alkaloids are organic basic substances isolated from plants. This name suggests that they are like alkali.

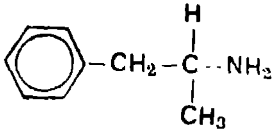
Serpasil is a powerful tranquilizer. It is obtained from an Indian plant, Raowolfia Serpentina, and its chemical name is reserpine. Extracts of Hashish and Charas also fall in this category of drugs



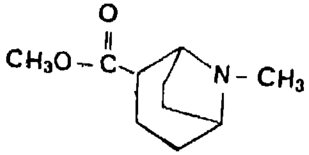
serpasil (reserpine)

21.5-6 ANTIDEPRESSANTS

These also act on the central nervous system and produce a feeling of well being and self confidence and may improve working efficiency of persons in depressed moods. They are thus called mood elevators They are incorporated in all sorts of pep pills These should not be taken without proper medical advice. Tofranil is one of such drugs Elevation of mood is also caused by amphetamine group of drugs. Typical example for these is benzedrine Large doses and persistent use of such drugs can lead to insanity Cocain, an alkaloid from Coca, can also produce similar effects when taken in small dozes.



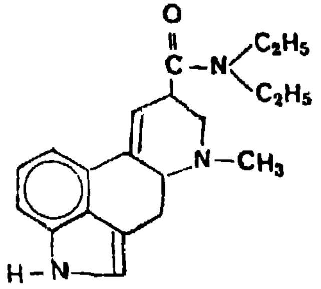
benzedrine (an amphetamine)



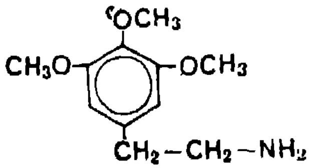
cocaine

21.5-7 PSYCHEDELIC DRUGS

These disturb vision and hearing, and cause hallucinations. Colours are observed where none exists One loses sense of space and time and gets a false feeling of happiness. A potent drug of this group is LSD-25 (lysergic acid diethylamide) and a some what less potent one is mescaline. These substances leave dangerous effects both on body and mind .As they are not sold in the open market, most samples we found to be contaminated with other dangerous substances. Many youngmen have been lost to society by their misguided use of these hallucinogenic drugs.



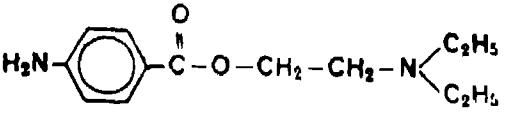
lysergic acid diethylamide (LSD)



mescaline

21.5-8 GENERAL ANAESTHETICS

Drugs which produce a general loss of sensation and consciousness are called general anaesthetics Some of these which act after absorption as vapours or gases from the lungs are diethyl and divinyl ethers, nitrous oxide, ethylene and cyclopropane. Some others are administered orally or injected into the body Amongst these are the narcotics, morphine, and pathedine The medicines applied or injected to cause senselessness in limited local areas as for tooth extraction and small surgical operations, are called local anaesthetics They create a benumbed feeling Examples are cocaine, novocaine, (procaine) and xylocaine which are injected or applied locally and ethyl chloride which is sprayed to cause intense cooling of the tissues to be operated upon

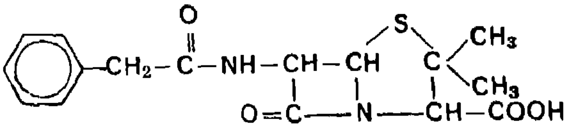


procaine

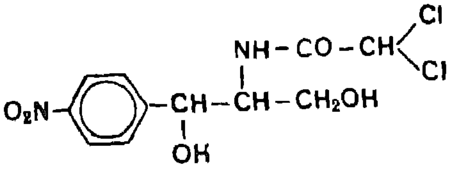
21.5-9 ANTIBIOTICS

These are chemotherapeutic substances which are obtained as metabolic products from some specific organisms (bacteria, fungi and moulds) and can be used to kill some other organisms. Being products of life processes and being used to stop other life processes, they have been given the group name of *antibiotics*. The first of the antibiotics discovered was penicillin which is a very effective drug for pneumonia, bronchitis, sore throat, abcesses, etc. Ampicillin is a semi synthetic modification of penicillin It is of more wider applications. Streptomycin is another well known antibiotic used for treatment of tuberculosis. Broad spectrum antibiotics are medicines which are effective against several different types of harmful micro-organisms

Amongst these are tetracyclins, chloramphenicols (chloromycetin), etc.

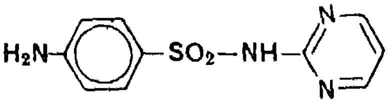


penicillin



chloromycetin (chloramphenicol)

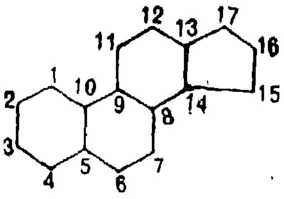
Sulpha drugs like sulphanilamide, sulphadiazine, sulphaguanidine and sulphacetamide act against micro-organisms like antibiotics and have been used in place of them.



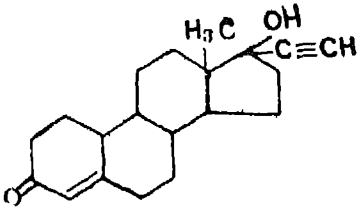
sulphadiazine

21.5-10 BIRTH CONTROL PILLS

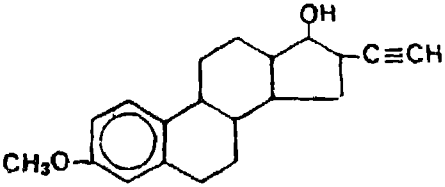
These contain drugs related to female sex harmones. These drugs have structures similar to the steroid ring structure A common brand name, Enovid E contains *norethynodrel* and *mestranol* All such medicines are likely to have side effects which may not have been observed so far and should be taken only under medical observation and guidance.



steroid ring structure



norethindrone



mestranol

EXERCISES

21. 1 Define the terms natural and synthetic polymers. State the uses of cellulose.

21. 2 State and explain the two methods by which synthetic polymers are made. Give examples and uses of any two synthetic polymers made by each method.

21. 3 What are chemical fertilizers ? State the advantages of urea and CAN over ammonium sulphate.

21. 4 (a) What are superphosphate and triple superphosphate ? How are they made ? Why is triple superphosphate preferred over ordinary superphosphate ?

(b) State why potassium sulphate is preferred to potassium chloride for tobacco plants.

21. 5 (a) Define the term "pesticide".

(b) What are DDT and BHC ? State the advantages and disadvantages of using them as insecticides.

(c) Give examples of organophosphate insecticides and explain their advantages over DDT and BHC.

21. 6 (a) Give examples of herbicides and explain the mechanism of their action.

(b) It is said that about 15 to 20 per cent of our total food crops are destroyed by rats. What cheap rodenticide do you suggest for this menace ?

21. 7 (a) What is a surface active agent ? How does it act ?

(b) Write the formula of a soap and explain the terms hydrophilic and hydrophobic groups.

21. 8 (a) What is meant by the term "synthetic detergent"?

(b) Write the structure of sodium dodecyl benzene sulphonate and state its advantages and disadvantages over ordinary soap.

21. 9 Define the term ; antiseptics, disinfectants and germicides. Give examples.

21.10 What are chemotherapeutic drugs ? Write the structure of aspirin and explain how it acts as a medicine.

21.11 Give examples of tranquillizers and explain their uses.

21.12 What are antibiotics ? Give examples.

Answers to Some Selected Questions

1.2	6.6×10^{-21} kg m sec^{-1}
1 3	2.475×10^{-19} J for 8000 Å, 4.95×10^{-19} J for 4000 Å
2 8	(b) 293.0 kJ mol^{-1}
3 4	0.42 nm
4 11	109 JK^{-1} mol^{-1}
4 12	462.7K
5.10	$t_{\frac{1}{2}} = 2.01 \times 10^{1}$ sec
5 11	$t_{\frac{1}{2}} = 9.43 \times 10^{3}$ sec
5 14	0.138 min^{-1}
6 2	$\chi_{C_2H_5OH} = 0.17$, χ_{H_2O} 0.83
6.3	0 008 mol litre^{-1}
6 4	$\chi_{H_2O} = 0.502$, $\chi_{C_2H_5OH} = 0.196$, $\chi_{CH_3COOH} = 0.30$
6.5	0.5 molal
6.10	(a) 110 mm Hg, (b) 80 mm Hg, (c) 114.1 mm Hg
6.11	(a) 373.018 K, (b) 272.934 K
6.13	46 g mol^{-1}
6.14	60.7 g mol^{-1}
6 16	288 g mol^{-1}
6.18	8 degree molal^{-1}
7.2	0 46 Volt
7.3	(a) 0.34 Volt, (b) = 1.10 Volt, (c) 1.08 Volt
7 7	(d) 0.93 Volt
1.5	6α, 4β
11 6	(a) 2.05 days (b) 14.1×10^{-6} kg, 10.2×10^{-6} kg, 5.02×10^{-6} kg
11.7	12.34%
11.8	(i) 4.256×10^{3} years, (ii) 53.31 years, (iii) 2.793×10^{9} years
11.9	$t_{\frac{1}{2}} = 25.1$ days, $\lambda = 0.02752$ days^{-1}
11.13	6.321×10^{24} atoms of C-14

Logarithm Table

	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170						5	9	13	17	21	26	30	34	38
						0212	0253	0294	0334	0374	4	8	12	16	20	24	28	32	36
11	0414	0453	0492	0531	0569						4	8	12	16	20	23	27	31	35
						0607	0645	0682	0719	0755	4	7	11	15	18	22	26	29	33
12	0792	0828	0804	0899	0934						3	7	11	14	18	21	25	28	32
						0969	1004	1038	1072	1106	3	7	10	14	17	20	24	27	31
13	1139	1173	1206	1239	1271						3	6	10	13	16	19	23	26	29
						1303	1335	1367	1399	1430	3	7	10	13	16	19	22	25	29
14	1461	1492	1523	1553	1584						3	6	9	12	15	19	22	25	28
						1614	1644	1673	1703	1732	3	6	9	12	14	17	20	23	26
15	1761	1790	1818	1847	1875						3	6	9	11	14	17	20	23	26
						1903	1931	1959	1987	2014	3	6	8	11	14	17	19	22	25
16	2041	2068	2095	2122	2148						3	6	8	11	14	16	19	22	24
						2175	2201	2227	2253	2279	3	5	8	10	13	16	18	21	23
17	2304	2330	2355	2380	2405						3	5	8	10	13	15	18	20	23
						2430	2455	2480	2504	2529	3	5	8	10	12	15	17	20	22
18	2553	2577	2601	2625	2648						2	5	7	9	12	14	17	19	21
						2672	2695	2718	2742	2765	2	4	7	9	11	14	16	18	21
19	2788	2810	2833	2856	2878						2	4	7	9	11	13	16	18	20
						2900	2923	2945	2967	2989	2	4	6	8	11	13	15	17	19
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4083	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8